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# Biodiesel production from non-edible plant oils

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Because of biodegradability and nontoxicity biodiesel has become more attractive as alternative fuel. Biodiesel is produced mainly from vegetable oils by transesterification of triacylglycerols. From economic and social reasons, edible oils should be replaced by lower-cost and reliable feedstocks for biodiesel production such as non-edible plant oils. This paper reviews various methods for biodiesel production from common non-edible oils employing alcoholysis reactions. The aim of this paper is to present the possibilities of the use of non-edible oils into biodiesel production, to consider the various methods for treatment of non-edible oils and to emphasize the influence of the operating and reaction conditions on the process rate and the ester yield. The special attention is paid to the possibilities of optimization, kinetics and improvement of biodiesel production from non-edible oils.



**Contents**



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## 1. Introduction

During the past decades worldwide petroleum consumption has permanently increased due to the growth of human population and industrialization, which has caused depleting fossil fuel reserves and increasing petroleum price. On the other hand, combustion of fossil fuels contributes most to emissions of greenhouse gases, which lead to atmospheric pollution and global warming. The transport section is almost utterly dependent on petroleum-derived fuels. The increase of the number of transport vehicles, as predicted [1], could affect the stability of environment and climate on the whole planet. Therefore, there is a great awareness in a diesel fuel substitution at the present all over the world with a clean, renewable fuel such as biodiesel, which has a lot of technical advantages over fossil fuels such as lower overall exhaust emission and toxicity, biodegradability, derivation from a renewable and domestic feedstock, negligible sulfur content, superior flash point and higher combustion efficiency. The biodiesel could be used as pure fuel or as blend with petrodiesel, which is stable in all ratios. Biodiesel production is expected to encourage employment and economic development in rural areas, to develop long term replacement of fossil fuels, to reduce national dependency on the petroleum import and to increase the security of energy supply [2].

Although biodiesel has a lot of advantages in related to petrodiesel, the high price of its production is the main barrier to its commercial use. Zhang et al. [3] showed that the price of biodiesel is about 0.5 US$/L, compared to 0.35 US$/L for petroleum diesel. Biodiesel price depends mainly on the cost of feedstocks, the price of which makes 70–95% of the total biodiesel cost [4–7]. The use of cheap non-edible oils can be a way to improve the economy of biodiesel production and its commercial production at the industry scale. Because of different climate conditions, various countries have been looking for various types of non-edible vegetable oils for possible use in biodiesel production.

Currently, edible oils are the main resources for world biodiesel production (more than 95%) [6]. However, there are many reasons for not using edible oils as feedstocks in biodiesel production. The use of edible oil in biodiesel production has an influence on the global imbalance to the market demand and the food supply by their high prices, the reduction of food sources and the growth of commercial plant capacities. Thus, focus should be shifted to non-edible resources, which are not used in the human nutrition and could grow in the barren lands. Oils from these resources are, as a rule, unsuitable for human consumption due to the presence of toxic compounds. For example, the main toxic compounds in jatropha plants are protein curcin and purgative agents, protein ricin in castor plant, glucoside cerberin in fruits of sea mango and flavonoids pongamiin and karajiin in karanja oil [6]. There are some other reasons for biodiesel production from non-edible oils, besides low cost and impossibility of their use for the human consumption. Firstly, there are many oil plants producing large amounts of non-edible oils in nature all over the world. Then, non-edible oil plants can be easily cultivated in lands unsuitable for human crops with much lower costs than those of the edible oil crops' plantation [6]. Finally, the growing of these plants reduces concentrations of $CO_2$ in the atmosphere [8]. However, as a serious drawback, most non-edible oils contain a high content of free fatty acids (FFAs), which increases the biodiesel production cost [7].

Chemically, biodiesel is the mixture of fatty acid alkyl esters (FAAEs), most often methyl or ethyl esters (FAMEs and FAEEs, respectively) obtained by the alcoholysis of triacylglycerols (TAGs) from vegetable oil and animal fats, or more precisely alcoholysis, with an alcohol (methanol or ethanol). In the reversible and consecutive alcoholysis reaction, one mole of acylglycerols reacts with one mole of alcohol and one mole of ester is formed at every step in the absence or presence of a catalyst. Alcoholysis of vegetable oil can be chemically or enzyme catalyzed. Chemical catalysts (base and acid) of alcoholysis can be homogeneous or heterogeneous, while the enzymes used as a catalyst are lipases. Non-catalytic alcoholysis reactions occur at high temperatures and pressures and still do not have any practical application.

A number of reviewing papers in the last few years indicate the importance of non-edible oils for the future biodiesel production. These papers have touched many relevant topics for the use of non-edible oils in biodiesel production. Balat and Balat [1], Demirbas [9], Kralova and Sjöblom [10] and Yusuf et al. [11] consider the different techniques to solve the problems encountered with the high fuel viscosity. Gui et al. [6], Demirbas [9], Karmakar et al. [8], Kumar and Sharma [12] and Balat [4] describe the physico-chemical characteristics of selected non-edible oil plants and their oils as well as esters produced from them. The engine performances of both non-edible oils and biodiesels produced from them have been reviewed in several reports [5,10,13–16]. Some review papers discuss different approaches of reducing the content of FFAs in various feedstocks via catalytic and non-catalytic transesterification [4,5,7,9,10,16–21]. The cost and environmental impact of biodiesel production processes is discussed by a few researchers [12,22]. A special attention has been paid to biodiesel production from jatropha oil in India, Malaysia and Indonesia [18,19,23–25]. However, the methods of biodiesel production, the impact of reaction conditions on the overall process rate and the ester yield as well as the optimization, kinetics and improvement of biodiesel production from non-edible oils have not yet attracted the attention they deserve. Murugesan et al. [26] analyze the effects of operation variables on the transesterification reaction of non-edible oils, while Leung et al. [7], Vyas et al. [21] and Shahid and Jamal [20] focus on specific processes for biodiesel production from different feedstocks such as Biox co-solvent, supercritical, microwave, ultrasound and in situ processes.

This paper is a review on various methods for biodiesel production from common non-edible oils employing alcoholysis reactions. The aim of this paper is to present the possibilities of the use of non-edible oils in biodiesel production, to consider the different methods for treatment of non-edible oils as alternative feedstocks and to emphasize the influence of some operating and reaction conditions on the process rate and the ester yield. The special attention is paid to the possibilities of optimization, kinetics and improvement of biodiesel production from non-edible oils.

## 2. Feedstocks and product characteristics

### 2.1. Types of feedstocks for biodiesel production

Feedstocks for biodiesel production can be traditionally categorized into three main groups [8]: vegetable oils (edible and non-edible), animal fats and waste cooking oils (used oily materials). Additionally, algal oils have been emerging in recent years as the fourth category of growing interest because of their high oil content and rapid biomass production [4,5,16,21,27].

Different kinds of vegetable edible oils, depending upon the climate and soil conditions, are being used as the main conventionally feedstocks for biodiesel production such as rapeseed oil in Canada, sunflower oil in Europe, soybean oil in US, palm oil in Southeast Asia, coconut oil in Philippines, etc. However, the rapidly growing world population and extensive human consumption of edible oils can cause some significant problems, for instance, starvation in developing countries. Therefore, non-edible plant oils become very promising alternative feedstocks for biodiesel production because of large demand for edible oils as food, the higher prices of edible oils than that of fossil fuels and the lower cost of non-edible oil plant cultivation. However, there will always be a competition between

**Table 1**
Oil content in seeds and kernels of some non-edible plants.

| Botanical name | Local name | Oil content, % | | References |
|---|---|---|---|---|
| | | Seed, wt.% | Kernel, wt.% | |
| *Jatropha curcas* | Jatropha, ratanjyot | 20–60 | 40–60 | [16] |
| *Pongamia pinnata* | Karanja, pungam | 25–50 | 30–50 | [16] |
| *Azadirachta indica* | Neem | 20–30 | 25–45 | [16] |
| *Madhuca indica* | Mahua | 35–50 | 50 | [12,16] |
| *Schleichera triguga* | Kusum | 10.65 | | [52] |
| *Ricinus communis* | Castor | 45–50 | | [16] |
| *Linum usitatissimum* | Linseed | 35–45 | | [16] |
| *Cerbera odollam* (*Cerbera manghas*) | Sea mango | 54 | 6.4 | [12,16] |
| *Gossypium* sp. | Cotton | 17–25 | | [53] |
| *Nicotiana tabaccum* | Tobacco | 36–41 | 17 | [54] |
| *Argemone mexicana* | Mexican prickly poppy | 22–36 | | [12,55] |
| *Hevea brasiliensis* | Rubber tree | 40–60 | 40–50 | [12,16] |
| *Melia azedarach* | Persian lilac | 10 | | [12] |
| *Simmondsia chinensis* | Jojoba | 45–55 | | [12,16] |
| *Thevetia peruviana* | Yellow oleander | 8.41 | 67 | [12] |
| *Moringa oleifera* | Moringa | 33–41 | 2.9 | [16] |
| *Thlaspi arvense* | Field pennycress | 20–36 | | [16] |
| *Euphorbia lathyris* | | 48 | | [56] |
| *Sapium sebiferum* | | 12–29 | | [56] |
| *Pistacia chinensis* | | 30 | | [57] |
| *Datura stramonium* | | 10.3–23.2 | | [58] |

edible and non-edible oily plants for land available. When deciding which type of oil crops should be grown, in addition to profits, their impact on the environment should also be taken into account [28].

There are a large number of oil plants that produce non-edible oils. From a list of 75 plant species containing oil in their seeds or kernels more than 30%, 26 species were reported by Azam et al. [29] as potential sources of the oil that can be employed for the synthesis of FAMEs suitable for the use as biodiesel. The advantages of non-edible oils as a diesel fuel are liquid nature portability, ready availability, renewability, lower sulfur and aromatic contents and biodegradability, while their disadvantages are higher viscosity, lower volatility and higher percentage of carbon residue as well as reactivity of unsaturated hydrocarbon chains [16].

In relation to vegetable oils, animal fats such as tallow, white grease or lard, chicken fat and yellow grease are often priced favorably for conversion into biodiesel, providing an economic advantage [30]. However, there is a limited amount of animal fats available, so they will never be able to meet the world's fuel needs. Besides, it is the fact that animal fats can create a big problem during the biodiesel production since they became solid wax at room temperature [31].

Waste cooking oils could be a good choice as feedstocks for biodiesel production because they are either priceless or cheaper than virgin vegetable oils (2–3 times) [32]. Their amount can be great in each country and is dependent on the use of vegetable oils from which they are generated. The transesterification process of waste cooking oils into alkyl esters reduces the molecular weight to one-third, the viscosity by about one-seventh and the flash point slightly, whereas the pour point is considerably increased [1]. Waste cooking oils can be contaminated by many types of impurities from the cooking process (polymers, FFAs, etc.) and their conversion to biodiesel is complicated. Many review papers are related to the use of waste cooking oils as feedstocks for biodiesel production [33–36].

The amounts of oily crops, both edible and non-edible, animal fats and waste cooking oils are limited, so it is unlikely to provide worldwide biodiesel production demand. The search for other renewable sources is needed to provide the required amount of oily feedstocks. In recent years a high interest has arisen towards producing biodiesel from microalgae. The advantages of microalgae using for biodiesel production are: much higher biomass productivities than land plants, some species can accumulate up to 20–50% TAG, no agricultural land is required to grow the biomass and they required only sunlight and a few simple and cheap nutrients [37].

### 2.2. The most-used non-edible oils for biodiesel production

Various oils extracted from seeds or kernels of non-edible crops are potential feedstocks for biodiesel production. The important non-edible oil plants are jatropha [38,39], karanja [38,40], tobacco [41–43], mahua [44,45], neem [46], rubber [47], sea mango [48], castor [49], cotton [50,51], etc. Of these feedstocks, jatropha, karanja, mahua and castor oils are the most often used in biodiesel synthesis.

In many countries, edible oils are not produced in enough amounts to meet the requirements for human use and must be imported. Hence, the price of biodiesel produced from edible oils is much higher than that of petrodiesel. An interesting case of biodiesel production from edible vegetable oils is India, where about 46% of the needed amounts for the domestic requirements are imported [23]. Therefore, non-edible oils from jatropha, karanja, neem, mahua and other plants are the only possibility for biodiesel production. Table 1 presents a summary on the oily plants and the oil contents of their seeds or kernels based on a wide literature survey. Only several, most important and most frequently used non-edible oils were selected for further discussion.

Jatropha plant is one of the most promising potential oil sources for biodiesel production in South-East Asia, Central and South America, India and Africa. Today, it is the major feedstock for production of biodiesel in developing countries like India, where the annual production is about 15,000 t [23]. It can grow almost anywhere, on waste, sandy and saline soils, under different climatic conditions as well as under low or high rainfall and frost. Its cultivation is easy, without intensive care and minimal effort. Its healthy life cycle of 30–50 years eliminates the yearly replantation. Jatropha oil content varies depending on the types of species, but it is about 40–60% in the seeds and 46–58% in the kernels [12]. Jatropha has comparable properties to diesel, such as calorific value and cetane number [59]. It has a great potential as an alternative fuel since it does not require any modification of the engine [23]. The serious problem with jatropha oil is its toxicity to people and animals [1].

Karanja is a nitrogen-fixing tree producing seeds with a significant oil content. It is a leguminous, medium size hardy tree with fast growing, which is native to India, the United States, Indonesia,

**Table 2**
Physico-chemical properties of methyl esters from different edible and non-edible oils.[a]

| Vegetable oil | Density, kg/m$^3$ | Kinematic viscosity at 40 °C, mm$^2$/s | Cetane number | Cloud point, °C | Flash point, °C | Oxidation stability at 110 °C, h |
|---|---|---|---|---|---|---|
| **Edible oils** | | | | | | |
| Linseed | 892 | 3.75 | – | −3.8 | – | 0.2 |
| Rapeseed | 882 | 4.44 | 54.4 | −3.3 | – | 7.6 |
| Sunflower | 880 | 4.44 | 49.0 | 3.4 | 183 | 0.9 |
| Soybean | 884 | 4.04 | 45.0 | 1.0 | 178 | 2.1 |
| Peanut | 883 | 4.90 | 54.0 | 5.0 | 176 | 2.0 |
| Palm | 876 | 5.70 | 62.0 | 13.0 | 164 | 4.0 |
| Rice bran | 885 | 4.96 | – | 0.3 | | 0.4 |
| Coconut | 807 | 2.73 | – | 0.0 | 110 | 35.5 |
| Olive | – | 4.50 | 57.0 | – | 178 | 3.3 |
| **Non-edible oils** | | | | | | |
| Castor | 899 | 15.25 | – | −13.4 | – | 1.1 |
| Jatropha | 880 | 4.80 | 52.31 | 2.7 | 135 | 2.3 |
| Karanja | | 4.80 | 55.84 | – | 150 | |
| Mahua | 850 | 3.98 | 56.61 | – | 208 | – |
| Neem | 884 | 5.21 | 57.83 | 14.4 | – | 7.1 |
| Tobacco | 888 | 4.23 | 51.6 | – | 165.4 | 0.8 |
| Standard EN14214 | 860–900 | 3.5–5.0 | >51 | 0.3 max | >101 | >6 |

[a] Based on the data taken from [6–8,10,16,29,54].

Australia, Philippines and Malaysia. Karanja oil has many toxic substances that do not allow its use as a cooking oil. Annual production of karanja oil in India is 55,000 t [23], of which only 6% is currently used [40]. It can be cultivated to improve the soil quality, and the exhausted land can be reused for the agricultural purpose [6].

Castor plant is easily grown as a weed and has similar ecological requirements as jatropha. It is native to India, China, Brazil, some countries of ex-USSR and Thailand. India produces about 0.73 Mt yearly, which is 60% of the world castor production [12]. Castor oil is completely soluble in alcohols and has a viscosity up to 7-times higher than that of other vegetable oils [60]. The high viscosity of crude castor oil is a problem for its direct use as a fuel.

Mahua and neem trees, medium to large trees found in most parts of India and Burma, are a significant source of oils. Almost the whole tree of neem is usable for various purposes in the medicine and as pesticides and organic fertilizer. The annual productions of neem and mahua oil in India are 100,000 t and 180,000 t, respectively [23]. Kernels of mahua contain up to 50% of oil [16], which contains about 20% FFAs making the procedure for biodiesel production from this oil very required [44].

The major regions of kusum tree production are located in India, Sri Lanka, Timor and Java. Bitter in taste and toxic, kusum oil has about 5–11% FFA. The pure oil cannot be used as a fuel because of its high viscosity. The production of kusum oil in India is 25,000 t/year [23].

Sea mango tree, well-known as a "suicide tree", grows in India, Madagascar, Malaysia, Sri Lanka and Cambodia. Having a high oil content (54%), its seeds are a worth source for biodiesel production, which has been used so far only in a transesterification process with a specific solid catalyst [48].

Greece and Turkey are two the main producers of cotton in the European Union and world. Cottonseeds are a source of one of the cheapest vegetable oil having extreme viscosity and high density. Refined cottonseed oil production in Turkey in 1997 was 20,546 t [61]. However, crop production is inconsistent according to harvest area and climatic conditions.

Several non-edible oils have been isolated from various plants all over the world such as *Moringa oleifera* [62–64], *Argemone mexicana* [55], *Thevetia peruviana* [65], *Thlaspi arvense* [66], *Euphorbia lathyris*, *Sapium sebiferum* [56], *Pistacia chinensis* bge [57] or *Datura stramonium* [58]. Beside many medicinal uses and significant nutritional value, *M. oleifera* oil has great potential for biodiesel production. After extraction of vitamin A and other high valuable constituents, the oil can be converted to biodiesel without any waste [63]. *T. arvense*, known as field pennycress or stinkweed, is native to North America and Eurasia. It is highly adapted to a wide variety of climatic conditions, tolerant of fallow lands and requires minimal agricultural inputs (fertilizer, pesticides, water). Meals from defatted seeds cannot be used as an animal feed because of high content of glucosinolate. Because of high oil content (20–36%), the field pennycress seeds are an acceptable feedstock for biodiesel production [66]. *E. lathyris* and *S. sebiferum* produce also significant amounts of oil in their seeds. Primarily, the both plants are native to China and adapted to alkaline, saline, droughty and acidic soils [56].

### 2.3. Comparison between alkyl esters of edible and non-edible oils

Some of the important physico-chemical properties of methyl esters produced from different edible and non-edible resources are shown in Table 2. A high density of esters from some edible (linseed) and non-edible (castor) oils is attributed to the presence of fatty acids having more than two double bonds [8]. However, having a higher content of saturated fatty acids, methyl esters produced from neem oil have a much higher cloud point than those produced from linseed oil. The high flash point of mahua biodiesel is due to the presence of esters with chains having more than 12 carbons. Coconut biodiesel has the smallest flash point. Further, biodiesel produced from some non-edible oils (jatropha, neem) has a small content of linoleic and linolenic acids, so its oxidation stability is higher than that of biodiesel from linseed oil. Due to the presence of saturated fatty acids, esters produced from coconut oil have the highest oxidation stability [8].

Some advantages of biodiesel fuel produced from various non-edible oil feedstocks, compared to diesel fuel, in compression ignition engines are shown in Table 3. The main advantages of the biodiesels are lower particulate matter, carbon monoxide, hydrocarbons, nitrogen oxides and smoke emission, higher compression ratio associated with higher injection pressure and higher diffusion combustion.

## 3. Transesterification methods for modification of non-edible oils into biodiesel

Vegetable oils can be converted into biofuel using four ways: blending, micro-emulsions, pyrolysis and transesterification [67,68]. The reversible transesterification reactions are the most

**Table 3**
The advantages of biodiesel fuel produced from various non-edible oils.

| Oil plant | Fuel advantages |
|---|---|
| Jatropha | Lower PM emission, higher compression ratio associated with higher injection pressure, higher diffusion combustion |
| Karanja | Lower $NO_x$ emission |
| Mahua | Lower CO, HC, $NO_x$ emissions, reduced smoke number |
| Rubber | Lower smoke emission |
| Neem | Lower CO, $NO_x$ and smoke emissions |

PM – particulate matter, $NO_x$ – nitrogen oxides, CO – carbon monoxide, HC – hydro carbon.

common method of converting TAGs from oils into biodiesel and the most promising solution of the high viscosity oil problem. The main factors affecting transesterification reaction and produced esters yield are: the molar ratio of alcohol:oil, type of alcohol, type and amount of catalyst, reaction temperature, pressure and time, mixing intensity as well as the contents of FFAs and water in oils.

The transesterification reaction can be non-catalyzed or catalyzed by an acid, a base or an enzyme. Depending on the solubility of the chemical catalyst in the reaction mixture, transesterification reaction can be homogeneously or heterogeneously catalyzed. These reactions can be accomplished as one-step (base or acid) or two-step (acid/base) processes, depending on the content of FFA. The latter process is recommended if a feedstock contains more than 1% of FFA [44], although some authors have recently suggested the content of 5% of FFA as the limit for process choice [69]. It should be mentioned that there is the method of transesterification that is performed under supercritical conditions.

### 3.1. Homogeneously catalyzed transesterification processes

Homogeneously catalyzed alcoholysis of non-edible oils via one- and two-step processes is the subject of the most researches on the FAAE synthesis and is the most frequently industrially applied biodiesel production. The feedstocks characteristics such as its FFA content and fatty acid composition influence dominantly the selection of the type of the biodiesel production process.

#### 3.1.1. One-step processes

The choice between base or acid catalysts mostly depends on the FFA content (or acid value) in the oily feedstock. The acid value of a feedstock is influenced by the oil source, the type of cultivation and the oil storage mechanism. Non-edible oils, generally, contain significant amounts of FFA that limit the use of high effective base catalysts. Wide ranges of acid value for non-edible oils can be found in the literature. For example, the acid value of jatropha oil varies from 0.92 mg KOH/g [70] to 28 mg KOH/g [7]. FFAs from oily feedstocks in the presence of base catalysts form soaps, which reduce FAME yield, cause catalyst loss and complicate phase separation. Base catalysts are preferable in the case of vegetable oils having a lower FFA content. Acid catalysts have low susceptibility to the presence of FFA in the oily feedstock due to their ability to simultaneously catalyze reactions of both FFA esterification and TAG alcoholysis. On the other hand, the acid catalyzed alcoholysis reaction is slow and long time is required to reach a high FAAE yield. Therefore, acid catalysts have been rarely applied in one-step processes.

Table 4 summarizes the catalyst type and the optimal reaction conditions for some homogeneously catalyzed (base and acid) alcoholysis of non-edible oils. Independently, of the type of catalyst, the alcoholysis reactions occur with the use of methanol or rarely ethanol at temperatures below the boiling point of alcohol. Sulfuric acid and alkali hydroxides (NaOH and KOH) are the most-used catalysts in transesterification processes. Almost in all reported studies the ester yield higher than 90% is achieved, independently of the type of used catalyst, alcohol and plant oil.

Beside a lot of advantages, the use of homogeneous catalysts has many drawbacks. Operating problems are related to the use of alkali hydroxides as a catalyst because they are hazardous [17]. Additionally, in order to meet the specified product quality, the process involves a number of washing and purification steps producing a large amount of wastewater, which is environmentally unfavorable and requires appropriate treatment. The high amount of water used in washing and consequent treatment of the resulting large effluent increases the overall process cost. For these reasons, homogeneously catalyzed alcoholysis could be considered as a traditional method for biodiesel synthesis, and alternative methods have been developed.

**Base catalysis**. Base catalyzed transesterification reaction is often used for biodiesel production from non-edible oils (Table 4). Base catalysts are highly catalytically active and low cost while biodiesel of high quality is obtained in a short reaction time [17]. The main disadvantages of base catalysts are the impossibility of converting FFA to alkyl esters and soap formation in the presence of FFA, which reduces the biodiesel yield and prevents glycerol separation [18].

The high biodiesel yield (higher than 90%) was achieved in the most of the studies, independently of the type of feedstock and alcohol. In the case of castor oil ethanolysis using sodium ethoxide as a catalyst and high alcohol:oil molar ratio (16:1), the highest ester yield of 99% was achieved [86]. Also, in the methanolysis reaction of jatropha and tobacco oils (the molar ratio 5.6:1 and 10:1, respectively) a high ester yield of 98% was obtained in 1.5 h [71] and 5 min [84], respectively. At the other side, very low yields of biodiesel were reported for jatropha [72,77] and sea mango [48] oils having a high FFA content.

So far, most researchers have used methanol and rarely ethanol for biodiesel production because the methanolysis is faster than ethanolysis and FAME yields are higher than those of FAEE yields. In the case of biodiesel production from castor oil, the maximum FAME yield of 90% is achieved in 1 h at 60 °C while the maximum FAEE yield of only 80% is obtained in 5 h at 80 °C [60]. However, a mixture of methanol and ethanol was used to produce biodiesel from jatropha oil in the presence of ultrasound [79]. In this way, the advantage of better oil solubility in ethanol than in methanol was used. Also, the mixed esters are a better solubility additive than methyl esters [79].

The alcohol:oil molar ratio usually used in the alcoholysis reaction of non-edible oils is 6:1 [42,60,76], although some researchers suggest a much higher molar ratio such as 10:1 [46,81,84] or even 113:6 [88]. The researchers generally agree that the increase of the initial alcohol:oil molar ratio increases the ester yield [62,72,81,83,84,89]. However, da Silva et al. [86] showed that the ester yield did not increase when the alcohol:oil molar ratio increased above the molar ratio of 16:1. In the case of castor oil ethanolysis, a high yield is obtained at higher ethanol:oil molar ratios and lower catalyst concentrations or at lower ethanol:oil molar ratios and higher catalyst concentrations, independently of the reaction temperature [60,86].

Most used base catalysts in transesterification processes are NaOH and KOH. The initial catalyst concentration is a very important factor influencing the TAG conversion degree. The optimal amount of the base catalyst is about 1% (based on oil weight), although some researchers have reported both slightly lower catalyst concentrations such as 0.5% [84], 0.7% [46] or 0.8% NaOH [73], and higher catalyst concentrations such as 3.3% NaOH [72] or 6% NaOH [60]. When the NaOH concentration was 3.3%, the maximum FAME yield was only 55%, which was explained by the coexistence of FFA in the oil [72]. The FFA content in crude jatropha oil was reduced from 3.1% to 0.25% in the presence of NaOH under the

**Table 4**
A review of the homogeneously one-step transesterification processes of different non-edible feedstocks.

| Feedstock (oil) | Type, volume of reactor, $cm^3$/Type of agitator, agitation intensity, rpm | Type of alcohol | Alcohol:oil molar ratio, mol/mol | Catalyst/loading, wt.% to the oil | Temperature, °C | Optimal reaction conditions | | Reference |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Reaction conditions | Yield (conversion), %/Time, min | |
| Jatropha | Flask, 1000/– | Methanol | 5.6:1 | NaOH/0.5–1.5 | 30–60 | 60 °C; 1% NaOH | 98/60 | [71] |
| | Pilot plant, 250[a]/– | Methanol | 5.6:1 | NaOH/0.5–1.5 | 30–60 | 60 °C; 1% NaOH | 96/90 | |
| | Glass tube, 15/Magnetic, 400 | Methanol | 0.1–0.7:1[b] | NaOH/0.5–3.0 | 65 | 0.7:1[b]; 3.3% NaOH | 55/120 | [72] |
| | Batch reactor, –/–, 300 | Methanol | 9:1 | NaOH/0.8 | 45 | | (96.3)/30 | [73] |
| | | Ethanol | 9:1 | NaOH/0.8 | 45 | | (93.14)/30 | |
| | – | Methanol | 12:1 | NaOH/1 | 65 | | 89.7[c]/7 | [74] |
| | Batch reactor, –/–, 5000 | Methanol | | KOH/– | 23 | | 68/120 | [75] |
| | Batch reactor, 224/Mechanical, 900 | Methanol | 6:1 | KOH/1 | 40–60 | 50 °C | 97.1/120 | [76] |
| | Flask, 500/Mechanical, 600 | Methanol | 6:1 | NaOH/1 | 60 | | 47.2[d]/60 | [77] |
| | | | 0.4:1[j] | $H_2SO_4$/1 | 60 | | 92.8[d]/240 | |
| | Double-necked flask, 100/Magnetic, – | Methanol | 3:1–10:1 | KOH/1 | 28 and 45 | 45 °C; 6:1 | (95)/180 | [78] |
| | | | | KOH/1 | 28 and 45 | 45 °C; 6:1 | (99)[e]/180 | |
| | Flask, 50/– | Mixture of methanol and ethanol 3:3 mol/mol | 6:1 | KOH/0.75 | | | 98[d]/7 | [79] |
| Jatropha | Pilot plant tank, –/ | Methanol | 6:1 | KOH/1 | 65 | | 91/180 | [80] |
| Karanja | Mechanical, – | Methanol | 6:1 | KOH/1 | 65 | | 89/180 | |
| Karanja | – | Methanol | 3:1 and 10:1 | KOH/1 | 45 and 60 | 10:1; 60 °C | (92)/90 | [81] |
| | | Methanol | 10:1 | KOH/1 | 60 | | (95)[e]/90 | |
| | – | Methanol | 27:1 | KOH/1[e] | 60 | | – | [82] |
| Neem | – | Methanol | 10:1 | NaOH/0.7 | 60–75 | | 88–94/6.5–8 h | [46] |
| | | Ethanol | 10:1 | | | | | |
| | Flask, –/–, 450–500 | Methanol | 4:1; 6:1; 8:1 | KOH/1–3 | 55, 60, 65 | 6:1; 60 °C; 2% KOH | 83.4/60 | [83] |
| Tobacco | Flask, 1000/– | Methanol | 6:1 | NaOH/<1.5 | 55 | | (86)/90 | [42] |
| | Flask, 1000/–, 600 | Methanol | 4:1–10:1 | KOH/0.5–1.5 | 40–60 | 10:1; 40 and 50 °C; 1% KOH | 98/5 | [84] |
| | | Methanol | 4:1–10:1 | NaOH/0.5–1.5 | 40–60 | 50 °C; 10:1; 0.5% NaOH | 98/5 | |
| Castor | Batch reactor, 250/Magnetic, – | Methanol | 6:1 | NaOH, KOH, $NaOCH_3$, $KOCH_3$/0.2[f] | 60 | $KOCH_3$ | 85/60 | [60] |
| | | Ethanol | 6:1 | | 80 | $NaOCH_3$ | 80/300 | |
| | Flask, 250/Magnetic, 600 | Ethanol | 12:1–20:1 | $NaOC_2H_5$/0.5–1.5 | 30–80 | 30 °C; 16:1; 1% | 93.1/30 | [85] |
| | Flask, 250/Magnetic, 400 (laboratory) | Ethanol | 6:1–39:1 | NaOH and $C_2H_5ONa$/0.5–1.5 | 30–80 | 30 °C; 16:1; 1% $C_2H_5ONa$ | (99)[e]/30 | [86] |
| | Batch reactor, 1000/Mechanical, 400 (large scale) | | 19:1 | NaOH/1 | 20–80 | 30 °C | 89.8/10 | |
| | Mechanical shaker | | 9.65:1–12.35:1 | KOH/1.33–2.17 | 30 | 11:1; 1.75% KOH | 80/90 | |
| Soybean and castor (25:75, w/w) | Batch reactor, 50/Magnetic, – | Methanol | 34:6 | NaOH/1:6[f] | – | | 87/1–10 h[g] | [87] |
| Cottonseed and castor (50:50, w/w) | | | | | | | 86/1–10 h[g] | |
| Castor | Batch reactor, 50/Magnetic, – | Ethanol | 34:6 | KOH/1:6[f] | – | – | 96/120 | [88] |
| Soybean and castor (75:25, w/w) | | | 34:6 and 113:6 | KOH/1:6[f] | – | 113:6 | 98/120 | |
| Sea mango | Flask, –/Magnetic, – | Methanol | 6:1 | NaOH/1 | 64.7 | | 8.3/60 | [48] |
| Cottonseed | – | Methanol | 6:1 | KOH/0.5–1.5 | 50–60 | 60 °C; 1.5% KOH | 91.4/30 | [50] |
| | | | | | | | 92.4[h]/7 | |
| | Batch reactor, 500/Mechanical, 600 and ultrasound[i] | Methanol | 7:1 | NaOH/1–2 | 60 | 2% NaOH | 95/20, 95[i]/20 | [51] |

Table 4 (*Continued*)

| Feedstock (oil) | Type, volume of reactor, $cm^3$/Type of agitator, agitation intensity, rpm | Type of alcohol | Alcohol:oil molar ratio, mol/mol | Catalyst/loading, wt.% to the oil | Temperature, °C | Optimal reaction conditions | | Reference |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Reaction conditions | Yield (conversion), %/Time, min | |
| | | Ethanol | 7:1 | NaOH/1–2 | 80 | 1; 2% NaOH | 86/60, 90[i]/60 | |
| | Flask, 1000/ Magnetic, 400 | Methanol | 3:1–9:1 | NaOH/0.5–1.5 | 60 | 6:1; 1% NaOH | 98.5/60 | [89] |
| Mahua | Double-necked flask, 100/Magnetic, – | Methanol | 3:1–10:1 | KOH/1 | 28 and 45 | 45 °C; 6:1 | (95)/180 | [78] |
| | | | | KOH/1 | 28 and 45 | 45 °C; 6:1 | (99)[e]/180 | |
| | Flask, 500/– | Methanol | 4.5:1–9:1 | $H_2SO_4$/1.0–7.0 | 65–70 | 9:1; 6% $H_2SO_4$ | | [90] |
| | | Ethanol | | | 80–85 | | 92/300 | |
| | | Butanol | | | 118–120 | | 95.4/300 | |
| Fodder radish | Kettle reactor, 1000/Mechanical, 500–3200 | Ethanol | 6:1–14:1 | $NaOCH_2CH_3$/0.9–1.5 | 36–60 | 30 °C; 6:1; 1.3% | 97.9/70 | [91] |
| Castor | Batch reactor, 250/Magnetic, – | Methanol | 6:1 | $H_2SO_4$/0.2[f] | 60 | | 85/480 | [60] |
| | | | | HCl/0.2[f] | | | 75/240 | |
| | | Ethanol | 6:1 | $H_2SO_4$/0.2[f] | 80 | | 65/240 | |
| | | | | HCl/0.2[f] | | | 75/480 | |
| *Moringa oleifera* | Beker, –/Magnetic, 400 | Methanol | 1:1–5:1[b] | KOH/0.5–1.5 | 30–60 | 60 °C; 3:1[b]; 1% KOH | 82/60 | [62] |

[a] Capacity, $dm^3$/day.
[b] w/w.
[c] Microwave irradiation.
[d] Ultrasonic power: 210 W.
[e] THF as co-solvent.
[f] Molar ratio.
[g] Average of different reaction times from 1 to 10 h.
[h] 21% of an exit microwave power of 1.2 kW.
[i] Ultrasonic power: 200 W; frequency: 24 kHz.
[j] v/v.

optimum reaction conditions [71]. NaOH neutralizes FFAs and induces soap formation, so an extra step is needed to remove the sodium soap after the reaction. If the NaOH concentration was decreased below or increased above the optimum, there was no significant change in the biodiesel yield [71]. Comparing the type of catalyst in the same operating conditions (alcohol type, temperature and alcohol:oil molar ratio), Parlak et al. [84] reported that the same ester yield was obtained using 1% KOH and 0.5% NaOH. Beside KOH and NaOH, potassium and sodium methoxides are also used as base catalysts. The catalytic efficiency of hydroxide ion was generally inferior to that of methoxide ion [60].

Different reaction times for completing the base catalyzed transesterification processes of non-edible oils have been reported. This process requires about 1.5–2 h, independently of the operating conditions, except much lower (5 min) [84] and much higher (5 h) [60] reaction times in the case of tobacco seed and castor oil, respectively. It is known that the conversion rate increases with the reaction time [92]. Chitra et al. [71] used four different reaction times in order to optimize the transesterification process of jatropha oil. Keeping methanol amount, catalyst concentrations and reaction temperature constant, the authors showed that the esters yield increased with reaction time. Furthermore, although the yield obtained by Tapanes et al. [73] is slightly lower than that reported by Chitra et al. [71], the reaction time is three times shorter.

The reaction temperature influences both the reaction rate and the yield of esters [92] and should be maintained below the boiling point of alcohol [93,94]. The optimal temperature for methanolysis of non-edible oils is about 60–65 °C, although some researchers recommend lower temperature such as 30 °C in the case of castor oil [86,95] and 50 °C in the case of jatropha [73,76], tobacco seed [42,84] and mahua oil [78]. In order to optimize the reaction temperature, some authors [71,82] have used different temperatures in the alcoholysis processes of non-edible oils, keeping alcohol amount, catalyst concentrations and reaction time constant. Their results clearly indicate that the ester yield proportionately increases with the increase in reaction temperature and the maximum yield of ester is obtained at 60 °C.

Chitra et al. [71] performed the biodiesel production on both laboratory- and large-scale after having optimized the concentration of alcohol, catalyst loading, reaction temperature and reaction time required for the transesterification of jatropha oil. Somewhat lower average ester yield was achieved by the large-scale production than in the laboratory conditions. Using castor oil, da Silva et al. [86] performed scale up with 8 times higher oil amount and found that the same ester concentration was obtained at both levels.

**Acid catalysis**. Besides many disadvantages like the slower reaction rate, the higher alcohol:oil molar ratio requirement, a lower catalyst activity and a need for higher process temperature, the use of acid catalyst in the transesterification reaction has some important advantages [19] such as the tolerance and less sensitivity towards the high FFAs presence in the low-cost feedstocks (> 6%) [21] and the possibility of simultaneously accomplishment of esterification and transesterification. The most used acid catalysts are sulfuric, phosphoric, hydrochloric, etc.

Biodiesel yield was up to about 90% in several studies related to acid-catalyzed transesterification (Table 4), but a much longer time was needed, compared to the base catalyzed process, except at high temperatures [60,77,90]. The type of alcohol, catalyst quantity and the reaction time are the factors that influence the ester yield [90].

### 3.1.2. Two-step (acid/base) processes

To take advantages of both base and acid catalysts, two-step (acid/base) processes for biodiesel production from non-edible oils with a high FFA content have been developed. The two-step process consists of acid catalyzed FFA esterification (pre-treatment) for reducing the FFAs (below 1%). The base catalyzed TAG alcoholysis is an effective way to achieve a high biodiesel yield within a short reaction time at mild reaction conditions, compared to one-step process. By using an acid catalyst (mainly sulfuric acid) in the first step of the process, the slow reaction problem is overcome, and the soap formation is eliminated. The only disadvantage of the two-step transesterification process is the higher production cost as compared to conventional, one-step process. A review of two-step homogeneously alcoholysis processes employing different non-edible oils are presented in Table 5. Important variables affecting the acid value in the first and the ester yield in the second step are the type of feedstock and alcohol, alcohol:oil molar ratio, catalyst concentration, reaction temperature and reaction time.

Crude and refined, deodorized jatropha oils containing the FFA 15% and 1%, respectively, illustrate the significance of the type of feedstock for biodiesel production. The FFA content of the former oil is far beyond the acceptable limit of base catalyzed transesterification, and the two-step process is the best way to utilize this oil. In addition, the refined deodorized jatropha oil has a much higher price than the crude oil. A comparison between the two different methods of biodiesel production shows that FAME yield achieved by the two-step acid/base-catalyzed esterification/transesterification is much higher (90%) than that obtained by the one-step base-catalyzed transesterification (55%) [72]. The similar results were reported by Deng et al. [77] working with jatropha oil with 10.45% of FFAs. In the base catalyzed process, due to saponification, the ester yield reduced significantly (down to only 47.2%), while a much higher ester yield (96.4%) was obtained in the two step process. To decrease the initial high FFA content in crude mahua oil below 1%, Ghadge and Raheman [44] carried out a two-stage pretreatment process of esterification catalyzed by sulfuric acid with removal of a methanol–water mixture by settling after each step. D'Oca et al. [103] have developed a novel base/acid procedure for the ethyl esters production from castor oil. The base catalyzed transesterification is used as the first step followed by the on pot addition of sulfuric acid, which improves the separation of FAEEs from glycerol because of breaking soap formation and increases FFAs yield in the esters' phase. At the end of the second step, the acid-catalyzed esterification of FFAs yielded more FAEEs. Afterward, the acid-catalyzed esterification of FFAs from the reaction mixture yields more FAEEs, compared to the conventional base catalyzed transesterification.

Methanol is the mainly used alcohol in both steps of the transesterification process. An exception is the biodiesel production from castor oil [101], where the optimal ethanol:oil molar ratio is much higher (40:1 and 20:1 in the first and second stage, respectively) than that in the methanolysis reaction of other non-edible oils. For the other non-edible oils, the reaction of methanolysis has been studied for different molar ratios, which are varied in the range of 6:1 to 18:1 in the both steps, independently of the type of catalyst. With increasing the molar ratio of methanol:oil in the first step, the acid value is sharply reduced at first, then decreases gradually and stays constant at the end [40,44,56,58,72,77,98], while the ester yield continuously increases [40,96]. The decrease of the acid value is due to the effect of water produced during the esterification of FFA, which prevents further reaction. Therefore, there is an optimum alcohol:oil molar ratio required to complete the esterification process. In the second step, relatively less amount of methanol is required for reducing the acid value, because some of FFAs have been already esterified during the first step, and less amount of water is produced during the reaction [44]. The low level of remained FFA from the first step affects the transesterification reaction. The esters yield increases to the optimal value and more or less remains the same with further increasing the methanol:oil molar ratio [38,43,52,56,58,96,97]. This is attributed to a more difficult separation of glycerol due to its emulsification with methyl esters [97].

**Table 5**
A review of the two-step (acid/base) catalyzed homogeneously transesterification processes of different non-edible feedstocks (I – first step: acid pretreatment, II – second step: base-catalyzed).

| Feedstock (oil) | Type, volume of reactor, cm$^3$/Type of agitator, agitation intensity, rpm | Step | Type of alcohol | Alcohol:oil molar ratio, mol/mol | Catalyst/loading, wt.% to the oil | Temperature, °C | Optimal reaction conditions | | Reference |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Reaction conditions | FFA conversion, %/Yield (conversion), %/Time, min | |
| Jatropha | | I | Methanol | 0.2:1–0.4:1[a] | $H_2SO_4$/1.3–1.6 | 60 | 1.43% $H_2SO_4$[a] | (92.8)/88 | [39] |
| | | II | Methanol | 0.15:1–0.25:1[a] | KOH/0.55[b] | 60 | 4:1 (0.16:1[a]) | 99/24 | |
| | Glass tube, 15/Magnetic, 400 | I | Methanol | 0.1:1–0.7:1[c] | $H_2SO_4$/1 | 50 | 0.6:1[c] | (93)/60 | [72] |
| | | II | Methanol | 0.5:1–3.0:1 | NaOH/1.4 | 65 | ca. 6.7:1, 0.24:1[c] | 90/120 | |
| | Flask, –/Magnetic, 1000 | I | Methanol | 3:1–12:1 | $H_2SO_4$/0.3–2 | 40–100 | 45 °C, 6:1, 0.5% $H_2SO_4$, | (93)/120 | [38] |
| | | II | Methanol | 3:1–12:1 | KOH/0.5–2.0 | 60 | 60 °C, 9:1, 2% KOH | 95/120 | |
| | Flask, –/Magnetic, 1000 | I | Methanol | 3:1–9:1 | $H_2SO_4$/0.25–1.5 | 40–100 | 45 °C, 6:1, 0.5% $H_2SO_4$ | (93)/120 | [96] |
| | | II | Methanol | 3:1–9:1 | KOH/0.5–2.0 | 40–100 | 60 °C, 9:1, 2% KOH | 95/120 | |
| | Batch reactor, 1500/–, 400 | I | Methanol | 2:8–2:3[a] | $H_2SO_4$/0.5–3 | 20–80 | 65 °C, 3:7[a], 1% $H_2SO_4$, | (95)/180 | [97] |
| | | II | Methanol | 3:7[a] | NaOH/0.5–3 | 20–80 | 50 °C, 3:7[a], 1% NaOH | 90.1/180 | |
| | Flask, 500/Mechanical, 600 | I | Methanol | 0.16:1–0.48–1[a] | $H_2SO_4$/1–6[a] | 60 | 0.4:1[a], 4% $H_2SO_4$[a] | (88.5)/60 | [77] |
| | | II | Methanol | 0.16:1–0.48–1[a] | NaOH/0.8–1.6 | 60 | 0.24–1[a], 1.4% NaOH | 96.4[d]/30 | |
| | Flask, 1000/Mechanical, 600 | I | Methanol | 8:1–10:1 | $H_2SO_4$/0.2–1.0 | 60 | 8:1, 0.4% $H_2SO_4$ | (92)/30 | [56] |
| | | II | Methanol | 6:1 | KOH/0.6–1.2 | 60 | 6:1, 1% KOH | 86.2/30 | |
| | Stock tank, 50 | I | Methanol | 0.16:1–0.4:1[a] | $H_2SO_4$/1–4[a] | – | 0.32:1, 3% $H_2SO_4$[a] | (91.4)/– | [98] |
| | | II | Methanol | 8:1 | NaOH/1.2 | – | – | (99.38)[e]/10 | |
| Jatropha[f] | Batch reactor, –/Mechanical, – | I | Methanol | | $H_2SO_4$/– | | | | [75] |
| | | II | Methanol | | KOH/– | 23 | | 73/120 | |
| Karanja | Flask, –/Magnetic, 1000 | I | Methanol | 3:1–9:1 | $H_2SO_4$/0.25–2 | 40–80 | 50 °C, 6:1, 1% $H_2SO_4$ | (94)/45 | [96] |
| | | II | Methanol | 3:1–9:1 | KOH/0.3–1.0 | 40–80 | 50 °C, 9:1, 0.5% KOH | 80/30 | |
| | – | I | Methanol | 6:1 | $H_2SO_4$/0.5 | 65 | | (91)/– | [40] |
| | | II | Methanol | 6:1 | KOH/1 | 65 | | 97/– | |
| | Flask, –/Teflon stirrer, 300 | I | Methanol | 0.1:1–0.5:1[c] | $H_2SO_4$/0.5–5 | | 33.83:1[c], 3.73% $H_2SO_4$ | (81.8)/3.17 | [99] |
| | | II | Methanol | 0.1:1–0.5:1[c] | KOH/0.5–1.5 | | 9.3:1 (33.4:1[c]), 1.33% KOH | 89.9[g]/2.5 | |
| | Jacketed reactor, 1000/Digital stirrer, 600–650 | I | Methanol | 6:1 | $H_2SO_4$/1 | 30 and 60 | 60 °C, 15:1 | (95)/– | [100] |
| | | II | Methanol | 6:1 | KOH/1 | 30 and 60 | 60 °C, 15:1 | (97)/60 | |
| Mixture of mahua and simarouba | Conical flask, 250/–, 230 | I | Methanol | Mahua oil: 0.34–0.36[a] | $H_2SO_4$/1.4–1.49[a] | | 19.37:1, 14.38% | –/59–90 | [45] |
| | | | | Simarouba oil: 0.27–0.40[a] | $H_2SO_4$/1.4–1.54[a] | | | –/40–90 | |
| | | II | Methanol | 5:1 | KOH | 60 | | 98/30 | |
| Kusum | Flask, 1000/Mechanical, 1200 | I | Methanol | 6:1–12:1 | $H_2SO_4$/0.5–1.25[a] | 40–64 | 50 °C, 10:1, 1% $H_2SO_4$[a] | (96)/60 | [52] |
| | | II | Methanol | 6:1–12:1 | KOH/0.5–1.1 | 40–65 | 50 °C, 8:1, 0.7% KOH | 95/60 | |
| Tobacco | Flask, –/Magnetic, 400 | I | Methanol | 4.5:1–18:1 | $H_2SO_4$/1–2 | 60 | 13:1, 2% $H_2SO_4$ | (94)/50 | [43] |
| | | II | Methanol | 6:1 | KOH/1 | 60 | | 91/30 | |
| Castor | Flask, 100/Magnetic, 300 | I | Ethanol | 40:1 | $H_2SO_4$/1 | 60 | | –/60 | [58] |
| | | II | Ethanol | 20:1 | KOH/1 | 60 | | (95.3)/60 | |
| | Flask, 100/Magnetic, 300 | I | Ethanol | 40:1 | $H_2SO_4$/1 | 60 | | –/60 | [101] |
| | | II | Ethanol | 20:1 | KOH/1 | 60 | | (95.6)[h]/60 | |
| Palm/rubber blend (1:1) | Flask, –/–, 360 | II | Methanol | 6:1–10:1 | KOH/0.5–2 | 45–65 | 55 °C, 8:1, 2% KOH | (96)/3 | [102] |
| *Datura stramonium* | | I | Methanol | 6:1–10:1 | $H_2SO_4$/0.4–1 | 60 | 8:1, 0.6% $H_2SO_4$ | (89)/30 | [58] |

Table 5 (*Continued*)

| Feedstock (oil) | Type, volume of reactor, $cm^3$/Type of agitator, agitation intensity, rpm | Step | Type of alcohol | Alcohol:oil molar ratio, mol/mol | Catalyst/loading, wt.% to the oil | Temperature, °C | Optimal reaction conditions | | Reference |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Reaction conditions | FFA conversion, %/Yield (conversion), %/Time, min | |
| | | II | Methanol | 6:1 | KOH/0.8–1.2 | 60 | 1% KOH | 87/30 | |
| *Thlaspi arvense* | Flask, 500/ Magnetic, 1200 | I | Methanol | 9.2:1 | $H_2SO_4$/1[a] | | | | [66] |
| | | II | Methanol | 6:1 | $NaOCH_2CH_3$/0.5 | 60 | | 94/90 | |
| [5pt] *Moringa oleifera* | | II | Methanol | 6:1 | $NaOCH_3$/1 | 60 | | –/60 | [64] |
| *Euphorbia lathyris* | Flask, 1000/ Mechanical, 600 | I | Methanol | 8:1–10:1 | $H_2SO_4$/0.2–1.0 | 60 | 10:1, 0.8% $H_2SO_4$ | –/45 | [56] |
| | | II | Methanol | 6:1 | KOH/0.6–1.2 | 60 | 6:1, 0.8% KOH | 86.2/30 | |
| *Sapium sebiferum* | Flask, 1000/ Mechanical, 600 | I | Methanol | 8:1–10:1 | $H_2SO_4$/0.2–1.0 | 60 | 8:1, 0.4% $H_2SO_4$ | –/30 | [56] |
| | | II | Methanol | 6:1 | KOH/0.6–1.2 | 60 | 6:1, 1% KOH | 88.3/30 | |

[a] v/v.
[b] w/v.
[c] w/w.
[d] Ultrasonic power: 210 W.
[e] Microwave power: 800 W. 2450 kHz, continuous process, flow rate: 5 (I step) and 3 mL/min (II step).
[f] *Jatropha gossypiifolia*.
[g] Microwave power: 180 W.
[h] In the presence of *n*-hexane as co-solvent.

Independently of the type of non-edible oil, a number of researchers have used sulfuric acid as an acid catalyst (the required amount varied from 0.4 to 5%) in the first stage and KOH or NaOH as a base catalyst (the required amount varied from 0.5 to 2%) in the second stage of the process. The catalyst amount affects the ester yield which firstly, increases and then starts to decline when the acid or base concentration increases above the optimal values (0.5% and 2%, respectively) [38,56,96,98]. A lower amount of acid catalyst than the optimal one in the first step does not reduce the acid value to the desired limit, whereas a higher amount results in darkening of the product [52,56,58]. Alternatively, when the transesterification of pretreated oils is carried out at a base catalyst concentration higher than the optimal one, the amount of soap generated during the reaction increases, and the ester yield is reduced [52,56].

Experiments with non-edible oils have been performed for various reaction times between 0.4 and 6 h. With the progress of the reaction up to the optimal reaction time, the FAME yield increases rapidly. In the acid-catalyzed pretreatment, when the reaction time is longer than the optimal one, the physical appearance and color of the oils become darker [56].

Most of researchers have been conducted their experiments at temperatures close to the boiling point of alcohol [38,52,96,97]. The maximum ester yield is obtained in the range of temperature from 50 to 60 °C. The reaction temperature for processing non-edible oils should be maintained below 60 °C because the saponification of TAGs by the base catalyst is much faster than the alcoholysis reaction [38,96]. Also, the base-catalyzed process at temperatures above 60 °C causes excessive methanol loss due to evaporation, reduces the overall ester yield [96] and increases the production cost [52].

All above-mentioned researches refer to the batch experiments with mechanical or magnetic agitators. There is only one two-step transesterification process, which is carried out in the continuous mode [98]. The high TAG conversion (about 99.4%) was obtained in a reactor with microwave irradiation. The reactor was developed to convert jatropha oil to alkyl ester using NaOH as a catalyst and to compare its performance with traditional reactors. It was concluded that the two-step continuous microwave process might find a practical application in the biodiesel production from non-edible oils.

### 3.2. Heterogeneously catalyzed transesterification processes

#### 3.2.1. One-step processes

A biodiesel synthesis by using heterogeneous (solid) catalysts is environmentally friendly because of a simple product separation and purification, which reduces the waste water amount. The additional benefit of the heterogeneous catalyst use is the possibility of their easy regeneration and reuse that make the biodiesel synthesis process cost-effective [104]. However, a major disadvantage of using heterogeneous catalysts is a low reaction rate caused by diffusion limitations in the three-phase (oil–alcohol–catalyst) reaction mixture [105], as well as the complex catalyst preparation followed by a significant contribution to the environmental impact in some cases. Recent researches have been focused towards low cost and eco-friendly heterogeneous catalysts with a high catalytic activity [106–109]. Generally, the preparation of this type catalyst involves washing, drying, crushing/powdering and calcinating at high temperatures.

Various compounds were investigated as heterogeneous catalysts for non-edible vegetable oils alcoholysis. Table 6 summarizes the catalyst type and the reaction conditions applied in heterogeneously catalyzed alcoholysis.

The catalytic activity of a heterogeneous catalyst depends on its nature, specific surface area, pore size and volume and active site concentration. The catalyst performance could be improved by

**Table 6**
The review of the catalyst type and reaction conditions applied in heterogeneously catalyzed alcoholysis of non-edible oils.

| Feedstock (oil) | Type, volume of reactor, $cm^3$/Type of agitator, agitation intensity, rpm | Alcohol | Alcohol:oil molar ratio, mol/mol | Catalyst/loading, wt.% to the oil | Temperature, °C | Optimal reaction conditions | | Reference |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Reaction conditions | Yield (conversion), %/Time, h | |
| Jatropha | Batch reactor Parr 4843, 50/Mechanical, 300 | Methanol | 4:1–14:1 | Montmorillonite KSF/1–20 | 80–180 | 12:1; 4.8%; 160 °C | 68/6 | [110] |
| | | | | Amberlyst 15/1–20 | | | 59/6 | |
| | Round-bottom flask, 50/Magnetic | Methanol | 9:1, 16:1, 20:1 | K/NaY zeolite (K loadings of 4, 8 and 12 wt.%)/4 | 65 | 16:1; 12 wt.% K on NaY | 73/3 | [111] |
| | Round-bottom flask, 150/Magnetic | Methanol | 5:1–25:1 | CaMgO/1–10 | 65 | 15:1; 4% | (83)/6 | [112] |
| | | | | CaZnO/1–10 | | | (81)/6 | |
| | Flask, 500/300–700 | Methanol | 3:1–15:1 | $KNO_3/Al_2O_3$/1–8 | 70 | 12:1; 6%; 600 rpm | (84)/6 | [113] |
| | Round-bottom flask, 50/ | Methanol | 55:1 | Mg–Zr mixed oxide with Mg/Zr weight ratios of 1:1, 2:1 and 3:1/10 | 30 and 65 | Mg/Zr = 2:1; 65 °C | ≈(100)/0.75 | [114] |
| | Batch reactor Parr 4842, 300/Mechanical | Methanol | 9:1–18:1 | $Mg_{0.7}Zn_{1.3}Al_{2/3}O_3$/1.5–10.5 | 150–190 | 11:1; 8.68%; 182 °C | 94/6 | [115] |
| | Flask, 100 | Methanol | 6:1–15:1 | CaO/0.5–2 | 50–70 | 9:1; 1.5%; 70 °C | (93)/2.5 | [116] |
| | Round-bottom flask/Mechanical, 300 | Methanol | 6:1 | CaO, Li–CaO; $La_2O_3$–ZnO; $La_2O_3/Al_2O_3$; $La_{0.1}Ca_{0.9}MnO_3$; CaO + $Fe_2(SO_4)_3$; Li–CaO+ $Fe_2(SO_4)_3$/5 | 60 | CaO + $Fe_2(SO_4)_3$; Li–CaO+ $Fe_2(SO_4)_3$ | ≈100/3 | [117] |
| | Round-bottom flask, 10 | Methanol | 1:2[a] | Mg/La mixed oxides with different Mg/La weight ratios/5 | Ambient and 65 | Mg/La = 3:1; 65 °C | ≈100/0.5 | [118] |
| Jatropha (pretreated) | Erlenmeyer flask, 25; Ultrasound 24 kHz, 200 W, Amplitude 30–70%, Pulse mode 0.3–0.9 s/s | Methanol | 5:1–15:1 | $Na/SiO_2$/1–5 | – | 50% amplitude; 0.7 s/s; 9:1; 3% | 98.5/0.25 | [119] |
| Jatropha | Flat bottom SS316 stainless steel reactor, 100/Magnetic, 170 | Methanol | 15:1 | Dodecatungestophosphoric (DTPA) supported on K-10 clay/5 | 170 | 20 wt.% DTPA/Clay | (93)/8 (93)/8 | [120] |
| Karanja | Round-bottom flask | Methanol | 3:1–15:1 | Li/CaO with Li ion amount from 1 to 3 wt.%/1–10 | 35–85 | Li/CaO with Li ion amount of 1.75 wt.%; 12:1; 5%; 65 °C | >99/2 >99/1 | [121] |
| Karanja | – | Methanol | 10:1 | Montmorillonite K-10; Hβ–Zeolite; ZnO/0.1 | 120 | ZnO | (83)/24 | [81] |
| | Parr reactor, 500/600 | Methanol | 6:1–15:1 | Li/CaO; Na/CaO; K/CaO/0.5–10 | 30–65 | Li/CaO; 12:1; 2%; 65 °C | 94.9–90.3[b]/8 | [122] |
| *Cerbera odollam* | Batch reactor | Methanol | 10:1 | Montmorillonite KSF/4; | 155 | $SO_4^{2-}/ZrO_2$/6; 8:1; 180 °C | 84/3 | [48] |
| | | | 8:1 | $SO_4^{2-}/ZrO_2$/6 | 180 | | | |

Table 6 (*Continued*)

| Feedstock (oil) | Type, volume of reactor, $cm^3$/Type of agitator, agitation intensity, rpm | Alcohol | Alcohol:oil molar ratio, mol/mol | Catalyst/loading, wt.% to the oil | Temperature, °C | Optimal reaction conditions | | Reference |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Reaction conditions | Yield (conversion), %/Time, h | |
| Castor | Batch reactor, 100/Magnetic | Methanol | 6:1–35:1 | $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$/5 | 40–60 | 29:1; 60 °C | 20/3 | [123] |
| | Stainless steel reactor | Methanol | 6:1 | $TiO_2/SO_4^{2-}$ with molar ratio $TiO_2/H_2SO_4$ of 5, 10 and 20/5[c] | 120 | $TiO_2/SO_4^{2-}$ with molar ratio $TiO_2$/H2SO4 = 5 | 25/1 | [124] |
| | Flask, 250/Mechanical; Flask, 250, Microwave (40 and 220 W) | Methanol | 6:1 | $SiO_2$/(30–50)% $H_2SO_4$; $Al_2O_3$/50% KOH/10 | Ambient and 60 | MW irradiation 40 W; $Al_2O_3$/50% KOH | (95)/0.08 | [125] |
| | | Ethanol | 6:1 | $SiO_2$/(30 and 50)% $H_2SO_4$/10 | | MW irradiation 40 W; $Al_2O_3$/50% $H_2SO_4$ | (>95)/0.33 | |
| | Round-bottom quartz flask, 250, Microwave (2.45 GHz, 220 W)/Magnetic, 600 | Methanol | 3:1–18:1 | (40–60)% $H_2SO_4$/C/1–7 | 55–70 | 12:1; 55% $H_2SO_4$/C; 5%; 65 °C | 94/1 | [126] |
| | Round-bottom quartz flask | | | | | | | [127] |
| | Conventional heating, 250/Mechanical, 600 | Methanol | 18:1 | $NaHSO_4{\cdot}H_2O$, $AlCl_3$, $Na_2CO_3$/7.5 | 65 | $Na_2CO_3$ | 79/4 | |
| | Microwave (2.45 GHz, 200–600 W)/Magnetic, 600 | Methanol | 6:1–30:1 | $NaHSO_4{\cdot}H_2O$, $AlCl_3$, $Na_2CO_3$/1.5–9.5 | 55–85 | $Na_2CO_3$; 18:1; 7.5%; 65 °C; 220 W | 90/2 | |
| Cottonseed | Autoclave, 250 | Methanol | 3:1–18:1 | $TiO_2$-$SO_4^{2-}$; $ZrO_2$-$SO_4^{2-}$/2 | 200–230 | $TiO_2$-$SO_4^{2-}$; 12:1; 230 °C | >90/8 | [128] |
| Cottonseed | Batch reactor, 250/Mechanical | Methanol | 6:1–18:1 | KF/γ-$Al_2O_3$ with KF-$Al_2O_3$ mass ratio of 20.21 to50.36%/1–5 | 50–68 | KF-$Al_2O_3$ mass ratio of 50.36%; 12:1; 4%; 65 °C | >90/3 | [129] |
| Used cottonseed | Round-bottom flask | Methanol | 3:1–15:1 | Li/CaO, Na/CaO, K/CaO with Li ion amount from 0.5 to 5 wt.%/1–8 | 35–75 | Li/CaO with Li ion amount of 1.5 wt.%; 12:1; 5%; 65 °C | >99/0.75 | [130] |
| Acidified cottonseed | Autoclave, 250/Magnetic | Methanol | 3:1–12:1 | $SO_4^{2-}/TiO_2$-$SiO_2$/1–5 | 180–220 | 9:1; 3%; 200 °C | 92/6 | [131] |
| Rubber seed<br>Jatropha<br>*Calophyllum* L. (pinnai)<br>Karanja | Teflon-lined steel autoclave, 100/rotating, 50 | Methanol | 15:1 | $K_4Zn_4[Fe(CN)_6]{\cdot}6H_2O{\cdot}2$(*tert*-BuOH)/3 | 170 | | (97)/8<br>(87)/8<br>(84)/8<br>(88)/8 | [132] |
| Yellow oleander | Batch reactor/Magnetic | Methanol | 20:1[d] | Ash of banana (*M. Balbisiana*) trunk | 32 | | 96/3 | [65] |
| *Moringa oleifera* | Pressurized batch reactor/350–360 | Methanol | 6:1–24:1 | $SO_4^{2-}/SnO_2$-$SiO_2$/3 | 60–180 | 19.5:1; 150 °C | 84/2.5 | [63] |

[a] Mass ratio.
[b] FFA content in oil from 0.48 to 5.75%.
[c] mol.% of catalyst to the oil.
[d] mL/g of oil.

catalyst support on the carriers, which provide a higher specific surface area [133] or by applying the appropriate pretreatment to increase the catalyst acidity or basicity [111,116,134]. The activity of heterogeneous catalysts is attributed to the presence of the large amount of strong basic [114,118,130], acid [132] or both basic and acid [115] sites. The catalytic activity of an impregnated catalyst depends on the type of the active catalyst as well as on the used catalyst precursor. Kumar and Ali [130] have reported that the activity of alkaline ion impregnated CaO depends on the metal ion type as well as on the metal salt used in the catalyst preparation. According to their results, Li/CaO obtained by impregnation of $Li_2CO_3$ possesses the highest surface area and basic strength, and consequently, the highest activity in the alcoholysis reaction.

The type of a heterogeneous catalyst for the biodiesel production from non-edible vegetable oils depends on the FFA content in the feedstock. The most often used non-edible oil in previous investigations of heterogeneously catalyzed alcoholysis is jatropha oil (Table 6). As expected, base catalysts are preferable in the case of oil with the lower FFA content [113,116,119]. Due to the acid solid catalysts' ability to simultaneously catalyze esterification and alcoholysis reaction, they are often used for FAME synthesis from non-edible oils with the high FFA content. Some researchers also employed the modified catalysts, which exhibited dual basic and acidic sites [111,115] or the mixture of acid and base catalysts [117], which allow oil conversion to biodiesel in a one-step process of simultaneous esterification and alcoholysis. The previous researches of heterogeneously catalyzed alcoholysis of non-edible oils have been aimed to develop a catalyst with a high catalytic activity. The most-used methods for the catalyst preparation are impregnation and co-precipitation usually by using metal nitrates, followed by drying and frequently calcination at a desired temperature.

The alkyl esters yield obtained in heterogeneously catalyzed alcoholysis is also influenced by the applied reaction conditions. Compared to homogeneously catalyzed reaction, the initial methanol:oil ratio, the catalyst loading and the reaction temperature are higher and the reaction time is much longer in order to achieve comparable esters yields. Generally, the optimal reaction conditions providing the highest alkyl esters yield must be experimentally determined.

Generally, the Mg/Zr mixed oxides with a Mg/Zr weight ratio of 2:1 [114], Mg/La mixed oxides with a Mg/La weight ratio of 3:1 [118], Li/CaO [121,130] and mixture of base (CaO and Li-CaO) and acid ($Fe_2(SO_4)_3$) catalysts [117] have the highest catalytic activity for non-edible oil methanolysis at mild reaction conditions. The total conversion of oily feedstock is achieved at 60–65 °C and within a relatively short reaction time (Table 6).

The major advantage of heterogeneous catalysts is the possibility of their reusing, which enables the continuous process development. Most researches of heterogeneously catalyzed alcoholysis deal with the catalyst reusability, and different results are obtained. $K_4Zn_4[Fe(CN)_6]\cdot 6H_2O\cdot 2$(*tert*-BuOH) [132], $SO_4^{2-}/TiO_2$-$SiO_2$ [131] and $TiO_2$-$SO_4^{2-}$; $ZrO_2$-$SO_4^{2-}$ [129] were stable catalysts, suitable for long-term use, but no catalyst regeneration methods are reported. Aluminum oxide-modified Mg–Zn catalyst ($Mg_{0.7}Zn_{1.3}Al_{2/3}O_3$) can be recycled five times with the drop in the FAME yield of 3% and 6% during regeneration and reusability from the first cycle, respectively [115]. An effective and stable heterogeneous catalyst is Mg–Zr mixed oxide, which is used in four cycles with a marginal decrease of the esters yield [114]. CaMgO and CaZnO are reused, after regeneration, three and four times, respectively, with maintaining the conversion higher than 80% [112]. However, in most cases, the heterogeneous catalysts are recycled up to three times after which a significant decrease in the FAME yield is observed [113,117,119,120]. Catalyst deactivation can be caused by three main reasons: product and by-product adsorption on the catalyst surface, the active sites leaching into the solution and the catalyst structure collapse [135]. In order to avoid the catalyst active sites blocking with organic residues or poisoning with atmospheric $CO_2$, researchers use different regeneration methods: washing with methanol and drying [114,115,119], washing with methanol and hexane followed by drying and calcination at a desired temperature [112], drying and calcination [113] and recycling the catalyst with glycerol [117].

The laboratory scale continuous process of heterogeneously catalyzed alcoholysis of non-edible oils was developed by Sreeprasanth et al. [132]. The process was conducted in a fixed-bed, down flow reactor. The catalyst ($K_4Zn_4[Fe(CN)_6]\cdot 6H_2O\cdot 2$(*tert*-BuOH)) was crushed, sized (10–20 mesh) and placed between ceramic beads into the reactor. The reactants (unrefined rubber seed oil and *n*-octanol at the alcohol:oil molar ratio 15:1) were fed using a syringe pump with the total flow rate 2 mL/h. The reaction was carried out at 170 °C under atmospheric pressure. The obtained rubber seed conversion was 89.2%, and no loss in the catalytic activity was noticed after 52 h [132]. Peng et al. [131] have proposed a continuous biodiesel production process from cheap raw feedstocks with the high FFA content, such as non-edible oils, soapstocks and waste cooking, oil by solid acid catalysis. The production process was carried out in a sequence of three reactors with a countercurrent flow of vaporized methanol. The excess methanol was recycled in a distillation tower, while the oil phase was refined at a biodiesel vacuum distillation tower. Using the proposed continuous process, a biodiesel demonstration production plant having an annual capacity of 10,000 t was built [131].

### 3.2.2. Two-step (acid/base) processes

Several studies deal with the use of heterogeneous catalysts in the two-step process (Table 7). The used oily feedstocks have high acid values between 10.5 mg KOH/g oil [135] and 24.76 mg KOH/g [139]. Heterogeneous catalysts are used either to catalyze FFA esterification or TGA alcoholysis. According to the best authors' knowledge, a completely heterogeneous two-step process has not been developed yet as a step is still homogeneously catalyzed.

The researches have been performed in the last few years to find a cheaper catalyst or a catalyst with a simple preparation method that reduces the biodiesel production cost. For example, CaO prepared from waste chicken eggshells by calcination is used as a catalyst in the two-step biodiesel production process from mahua [138] and karanja [137] oil, and the FAME yields of 95% are achieved. The simple calcination is used for preparing $SO_4^{2-}/TiO_2$ [136] and $SO_4^{2-}/ZrO_2$ [139], which are effective catalysts for FFA esterification reaction in a two-step process providing 9% and 94% FFA conversion, respectively. As in the case of one-step process, catalyst reuse is attractive from the point of the continuous process development. CaO [138] and hydrotalcite with Mg/Al molar ratio 3:1 [135] are reused for 10 runs after washing and calcination and for 8 runs after washing with ethanol, respectively, without any significant loss in the FAME yield. The best reusability performance is shown in the case of $SiO_2\cdot HF$, which is recycled 30 times without the catalyst regeneration and with the unchanged FAME yield [134].

## 3.3. Enzyme-catalyzed transesterification processes

It is well-known that lipases, enzymes that catalyze both transesterification and esterification reactions, have a high catalytic activity in water-poor media. Therefore, lipase-catalyzed transesterification reaction is carried out in non-aqueous environments such as solvent-free systems, organic and ionic liquids, gaseous media and supercritical fluids. The advantages of this process are simultaneously catalysis (TAG alcoholysis and FFA esterification), easy recovery of glycerol, the use of feedstock with high FFA

**Table 7**
The review of the catalyst type and reaction conditions applied in two-step heterogeneously catalyzed alcoholysis of non-edible oils (I – first step: acid pretreatment, II – second step: base-catalyzed).

| Feedstock (oil) | Type, volume of reactor, $cm^3$/Type of agitator, agitation intensity, rpm | Step | Alcohol | Alcohol:oil molar ratio, mol/mol | Catalyst/loading, wt.% to the oil | Temperature, °C | Optimal reaction conditions | | Reference |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Reaction conditions | Yield (conversion), %/Time, h | |
| Jatropha | Three-neck flask, 250/Mechanical | I | Methanol | 1–14[b] 1:1–30:1[c] | $H_2SO_4$/1 $SO_4^{2-}/TiO_2$/1–5 | 30–70 70–140 | 12 wt.%; 70 °C 20:1; 4%; 90 °C | (≈91)[a]/1 (≈97)[a]/2 | [136] |
| | Autoclave/Mechanical, 1500 | II | Methanol | 6:1 | KOH/1.3 | 64 | | 98/0.33 | |
| | Flask, 1000/Magnetic, 400 | I | Methanol | 3:1–12:1[c] | $SiO_2 \cdot HF$/2–15 | 50–60 | 12:1; 10%; 60 °C | (96)[a]/2 | [134] |
| | | II | Methanol | 6:1 | NaOH/1 | 60 | | ≈99.6/2 | |
| | Three-neck flask, 500 in ultrasound reactor 180–270 W/Mechanical, 600 | I | Methanol | 40[e] | $H_2SO_4$/4[d] | 60 | | (≈88)[a]/1 | [135] |
| | | II | Methanol | 3:1–6:1 | Hydrotalcite with Mg/Al molar ratio 3/1/0.5–1.25 | 40–55 | 210 W; 4:1; 1%; 45 °C | 95/1.5 | |
| Karanja | Round-bottom flask, 1000/Mechanical, 150–900 | I | Methanol | 6:1 | $H_2SO_4$/1.5, v/v | 65 | – | (≈91)[a]/1 | [137] |
| | | II | Methanol | 6:1–12:1 | CaO (obtained from chicken eggshells)/1–3.5 | 45–75 | 8:1; 2.5%; 65 °C; 600 rpm | 95/2.5 | |
| Mahua | Round-bottom flask, 1000/Mechanical, 1000 | I | Methanol | 6:1–12:1 | $H_2SO_4$/0.5–2, v/v | 45–65 | 6:1; 1.5 (v/v); 55 °C | (91)[a]/1 | [138] |
| | | II | Methanol | 5:1–9:1 | CaO (obtained from chicken eggshells)/1.5–3.0 | 45–70 | 8:1; 2.5%; 65 °C | 95/2.5 | |
| Neem | Round-bottom flask/Mechanical | I | Methanol | 3:1–12:1 | $SO_4^{2-}/ZrO_2$/0.5–1.5 | 30–90 | 9:1; 1%; 65 °C | (≈94)[a]/2 | [139] |
| | | II | Methanol | 6:1 | KOH/1 | 60 | | 95/2 | |

[a] FFA conversion.
[b] wt.% of methanol to the oil.
[c] methanol:FFA molar ratio.
[d] vol.% of $H_2SO_4$ to the oil.
[e] vol.% of methanol to the oil.

content and a minimal quantity of waste water generated. The main drawback in the use of the enzyme-based process is the high price of the enzyme. To obtain a reusable enzyme catalyst for the continuous processes, lipases are usually immobilized, which enables their recycling, easy recovery and lower costs. The lipase origin is the main factor which influences the ester yield. The immobilized lipases from different origins, such as *Candida antractica* [49,140–146], *Chromobacterium viscosum* [146,147], *Mucor miehei* [49], *Pseudomonas cepacia* [148,149], *Pancreatic* [150] and *Rhizomucor oryzae* [144,151], are most frequently used in non-edible oil alcoholysis reactions. Generally, enzyme-catalyzed alcoholysis is performed with a high lipase amount (about 5–30%). Celite, macroporous acrylic resin, macroporous anion exchange resin, silica and reticulated polyurethane foam are the most often used carriers for immobilized enzyme. In the case of ethanolysis of jatropha oil catalyzed by immobilized lipase of *Chromobacterium viscosum* [147] and *Pseudomonas cepacia* on Celite 545 [149] the FAEE yield is increased, compared to that achieved by freely suspended lipase.

However, lower linear alcohols, such as methanol and ethanol, conventionally used in the biodiesel process, can deactivate immobilized lipases [140]. Ethanol is more facile in the enzyme-catalyzed reaction than methanol due to a lower lipase deactivation degree. Some authors have suggested the use of propan-2-ol, ethyl acetate [140] or diethyl carbonate [152] as acyl acceptors in the biodiesel production from non-edible oils to overcome lipase inactivation. The other solutions include the stepwise addition of methanol [57,144,145] and the use of organic solvent such as hydrophobic *n*-hexane [49,153] or hydrophilic *t*-butanol [142,150]. Approximately, the same ester yields are achieved in the presence and absence of an organic solvent [148]. However, the use of solvent enables a significant advantage of higher reaction rate. Otherwise, Chattopadhyay et al. [150] have tested four different solvents: hexane, acetonitrile, toluene and *t*-butanol. The last one is most suitable due to good solubility of all reactants and products into it and the highest conversion achieved. Anyway, the use of solvent in biodiesel production is not generally recommended for reasons of safety and economy. The repeated use of immobilized enzyme is the important way to decrease the cost of product [154]. The review of the reaction conditions of the lipase-catalyzed alcoholysis which provide a significant ester yield is given in Table 8.

The optimum temperature for enzymatic transesterification is determined by the lipase stability and the reaction rate [155]. Generally, the enzymatic reaction is performed at temperatures between 30 and 50 °C, except the lipase-catalyzed alcoholysis of castor oil, which occurs at 65 °C [49]. Water is a very important factor in the enzyme-catalyzed process, because it influences the lipase catalytic activity and stability, contributing to the higher ester yield. Also, the water amount plays another important role influencing the esters hydrolysis, which decreases the esters yield. According to numerous studies with *Candida antractica* [49,140–143,145], the high ester yield is achieved in the absence of water. Immobilized lipase is operationally stable over twelve repeated cycles of alcoholysis using propan-2-ol and ethyl acetate as acyl acceptors [140,141]. There is no significant loss in the lipase activity in the both cases due to better miscibility of propan-2-ol and ethyl acetate in TAG and their less polarity than linear chain alcohols.

Batch laboratory reactors (types of vial, Erlenmeyer or flask) have been mainly used for enzymatic biodiesel production from non-edible oils. Only in a study [142], a one-step continuous packed bed reactor has been reported to operate over 500 h without substrate conversion loss, which is a very important result for the practical process application. The main disadvantage of this process is the necessity of solvent recovery.

### 3.4. Supercritical transesterification processes

The transesterification of non-edible oils by alcohols (methanol, ethanol, propanol and butanol) under supercritical conditions has been considered to be the most promising process for biodiesel production. In this way, the initial reaction lag stage caused by the low solubility of the alcohol in the oil phase can be overcome, the reaction rate is higher, the reaction time is shorter, separation and purification of biodiesel are simply, there are no soap formation and no waste generation from catalyst separation and absence of catalyst makes the glycerol recovery easier. The main disadvantages of supercritical reaction are the easy degradation of produced esters at an extremely high temperature and the high cost of the apparatus. The additional drawbacks are the high pressure and temperature and the large amount of alcohol used [18]. Co-solvents and subcritical alcohol could be added into reaction mixture to reduce the operating costs [21].

The review of the operating conditions applied in supercritical one- and two-step processes in various batch and continuous reactors is given in Table 9. A higher alcohol:oil molar ratio is required to push non-catalytic supercritical alcoholysis forward and to complete conversion when oil contains a high FFA amount [157]. The yield of produced esters increased with increasing the molar ratio of alcohol to oil [61,157,158,161,162], perhaps due to the increased contact area between alcohol and TAG. A 100% FAME yield was achieved in the case of lower content of FFA (only 2%) in the feedstock, compared to those obtained with the oils with higher FFA contents [158].

Similar results are obtained by the transesterification of non-edible oils with supercritical methanol and ethanol [161–163]. Both alcohols have similar reactivity at the supercritical temperature and produce similar contents of the esters. However, the conversion degree is higher with supercritical methanol than with supercritical ethanol [9,61].

Few researchers have studied the effect of the reaction temperature and pressure on supercritical alcoholysis. The increase of the reaction temperature favorably influences the ester yield, independently of the type of feedstock [9,61,156,158,161–163]. The common reaction temperature is higher than the critical temperatures of methanol (240 °C) and ethanol (244 °C). Also, approximately the complete TAG conversion can be achieved at a pressure of 20 MPa [157,161,162]. The increase of the reaction pressure influences the ester yield [157,158]. This effect is probably due to the increase of the density with increasing the pressure, which causes an increase in the solvent power of the supercritical fluid [157]. In the reaction of crude jatropha oil with micro-NaOH under the pressure ranging from 4 to 14.5 MPa, only a little difference in the ester yield is observed [156]. Some researchers have shown that the conversion under supercritical conditions is completed in a very short time and there was no separation problem [157,158] inherent to conventional catalytic processes.

Recently, some researchers have applied a novel two-step process as a promising alternative to the one-step supercritical method. It consists of the hydrolysis of TAGs in subcritical water (on 270 °C) and the subsequent supercritical esterification of the produced and separated fatty acids non-catalytically in supercritical methanol [159,160] or dimethyl carbonate [69]. In this way, the FAME yield was increased, compared to the conventional base-catalyzed method. Also, a more valuable by-product, glyoxal, is produced instead of glycerol, which is not affected by the high FFA content [69]. Also, this product is a non-acidic one and does not to deteriorate a feedstock with a high content of poly-unsaturated fatty acids. However, the cost of dimethyl carbonate is much higher than that of methanol or ethanol.

In the transesterification of non-edible oil with supercritical methanol in the presence of micro-NaOH as the catalyst, a high yield

**Table 8**
The review of the reaction conditions of the lipase-catalyzed transesterification processes of different non-edible feedstocks.

| Feedstock (oil) | Type, volume of reactor, $cm^3$/Type of agitator, agitation intensity, rpm | Type of alcohol | Alcohol:oil molar ratio, mol/mol | Lipase source (enzyme commercial name) | Carrier | Lipase loading, wt.% to the oil | Temperature, °C | Solvent | Water, wt.% to the oil | Optimal reaction conditions | | Reference |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | Reaction conditions | Yield (conversion), %/Time, h | |
| Jatropha | Screw capped vessel, 50/Reciprocating, 150 | Methanol | 0.5:1–4:1 | *Rhizopus oryzae* | Reticulated polyurethane foam | 1–10 | 30 | – | 0–10[b] | 1:1, 6, 5[b] | 80/60 | [144] |
| | | | 0.5:1–4:1 | *Candida antractica* (Novozym 435) | Macroporous acrylic resin | 1–10 | 30 | – | – | 1:1, 2 | 76/90 | |
| | Erlenmeyer type flask, 25/– | Methanol | 3:1–5:1 | *Chromobacterium viscosum* | Silica activated with ethanolamine | 3–6 | – | – | – | 4:1, 5 | (84.5)[c]/0.5 | [146] |
| | Screw capped vial, –/Reciprocal, 200 | Methanol | 1:1–5:1 | *E. aerogenes* | Silica activated with ethanolamine | 20–60 U | 30–55 | *t*-butanol | 5–20[b] | 4:1, 50, 55 °C, 0 | 94/60 | [154] |
| | Screw capped vial, 10/–, 180 | Diethyl carbonate | 1.5:1–7.5:1 | *Candida antractica* (Novozym 435) | | 5–15 | 45 | – | 0–3 | 3.75:1, 13.7, 0 | 96.2/13.3 | [143] |
| | Screw capped vial, –/–, 200 | Ethanol | 4:1 | *Chromobacterium viscosum* | Celite-545 | 10 | 40 | – | 0–2[a] | 0.5[a] | 92/8 | [147] |
| | Screw capped vial, –/–, 200 | Ethanol | 4:1 | *Pseudomonas cepacia* | Celite | 10 | 50 | – | 4–5 | 5 | (98)/8 | [149] |
| Jatropha<br>Karanja | Screw capped tube, –/Magnetically, 150 | Propan-2-ol | 1:1–5:1 | *Candida antractica* (Novozym 435) | Macroporous acrylic resin | 5–30 | 50 | – | – | 4:1, 10 | (92.8)/10<br>(91.7)/10 | [140] |
| Jatropha<br>Karanja | Screw capped tube, –/Magnetically, 150 | Ethyl acetate | 3:1–13:1 | *Candida antractica* (Novozym 435) | Macroporous acrylic resin | 5–30 | 50 | – | – | 11:1, 10 | 91.3/12<br>90/12 | [141] |
| Castor | Erlenmeyer type flask, 300/–, 200 | Ethanol | 3:1–10:1 | *Candida antractica* (Novozym 435) | Macroporous acrylic resin | 5–20 | 35–65 | *n*-hexane | 0–10 | 10:1, 20, 65 °C, 0 | (81.4)/6 | [49] |
| | | | | *Mucor miehei* (Lipozyme IM) | Macroporous anion exchange resin | | | *n*-hexane | | 3:1, 20, 65 °C, 0 | (98)/6 | |
| Mahua | Screw capped vial, 5/–, 200 | Ethanol | 4:1 | *Pseudomonas cepacia* | $K_2SO_4$ microcrystals<br>Glutaraldehyde<br>Polypropylene | 10 | 40 | – | 2–10 | 6 | (99)/2.5<br>(92)/2.5<br>(96)/6 | [148] |
| Cottonseed | Fixed bed batch reactor | Methanol | 1.5:1–6:1 | *Candida antractica* (Novozym 435) | Macroporous resin | 1.7 | 25–50 | *t*-butanol | | 6:1, 50 °C | 97/24 | [142] |
| | Fixed bed continuous reactor[d] | Methanol | 6:1 | *Candida antractica* (Novozym 435) | Macroporous resin | | 50 | *t*-butanol | | | 95/500 | |
| | Screw capped vessel, 50/Reciprocating, 150 | Methanol | 38:1–1:10 | *Candida antractica* (Novozym 435) | | 3.5 | 40 | – | | 4:1 | 95 | [145] |
| | –, –/–, 180 | Methanol | 1:1–25:1 | Pancreatic | | 0.05–3 | 25–50 | *t*-butanol | 0–30 | 15:1, 0.5, 37 °C, 5 | 75–80/4 | [150] |
| Rice bran | Flask, 50/Reciprocating, 170 | Methanol | 4:1–1:3 | *Candida sp.* 99–125 | | 20 | 30–60 | *n*-hexane | 0–60 | 2:1, 40 °C, 20 | 87.4/12 | [153] |
| *Pistacia chinensis* bge | Shaking flask, 25/–, 160 | Methanol | 3:1–6:1 | *Rhizopus oryzae* (F-AP15) | Macroporous resin and anion excange resin | 7[e] | 30–45 | – | 0–80 | 5:1, 37 °C, 20 | 94/60 | [57] |

[a] w/v.
[b] v/v.
[c] Ultrasonic: 200 W, 24 kHz.
[d] Enzyme flow rate: 9.6 mL/h.
[e] IU/g.

**Table 9**
A review of the optimal operating conditions applied in supercritical transesterification processes of different non-edible feedstocks.

| Feedstock (oil) | Type, volume of reactor, $cm^3$/Type of agitator, agitation intensity, rpm | Type of acyl acceptor | Acyl acceptor (Water):oil molar ratio, mol/mol | Catalyst/loading, wt.% to the oil | Temperature, °C | Pressure, MPa | Optimal reaction conditions | | Reference |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Reaction conditions | Yield (conversion), %/Time, min | |
| Jatropha | Cylindrical autoclave, 250/Magnetic, 400 | Methanol | 18:1–36:1 | Micro NaOH/0.2–0.8 | 240–270 | 4–14.5 | 250 °C, 7 MPa, 24:1, 0.8% NaOH | 90.5/28 | [156] |
| | Stainless steel vessel, 100/–, 960 | Methyl acetate | 25:1–59:1 | – | 300–345 | 10–30 | 345 °C, 20 MPa, 42:1 | (100)/50 | [157] |
| | Bench-scale reactor, 3700/Mechanical, – | Methanol | 10:1–43:1 | – | 239–340 | 5.7–8.6 | 320 °C, 8.4 MPa, 43:1 | 100/4 | [158] |
| | | I step: Water<br>II step: Dimethyl carbonate | I:217:1<br>II:14:1 | – | I: 255–350<br>II: 270–350 | I: 25–32<br>II: 6–19 | I: 270 °C, 27 MPa<br>II: 300 °C, 9 MPa | I: –/25<br>II:97/15[a] | [69] |
| | Tubular reactor, 1000/– | I step: Water<br>II step: Methanol | I: –<br>II:3:1[b] | – | I: 250–290<br>II: 250–290 | I: 11<br>II: 11 | I: 270 °C<br>II: 290 °C | I: (92.1)/60<br>II:(99)/15[a] | [159] |
| | Tubular reactor, 1000/– | I step: Water<br>II step: Methanol | I: 10:1[b]<br>II: 3:1–7:1[b] | – | I: 250–310<br>II: 250–290 | I: 11<br>II: 11 | I: 290 °C<br>II: 290 °C, 3:1 | I: (94.8)/60<br>II:(98.3)/9[a] | [160] |
| Jatropha | Batch reactor, 11/– | Methanol | 10:1–70:1 | – | 200–400 | 20 | 400 °C, 50:1 | (95)/30 | [161] |
| | | Ethanol | 10:1–70:1 | | 200–400 | | | (94)/20 | |
| Karanja | | Methanol | 10:1–70:1 | | 200–400 | 20 | 400 °C, 50:1 | (95)/20 | |
| | | Ethanol | 10:1–70:1 | | 200–400 | | | (94)/30 | |
| Jatropha | Batch reactor, | Methanol | 1:1–6:1 | Novozym 435, in SC $CO_2$, 10–70 | 30–60 | 6.8 | 45 °C, 5:1, 30% | (≈48)/600 | [161] |
| | 7/– | Ethanol | | | | | | (55)/600 | |
| Karanja | | Methanol | | | | | | (≈48)/600 | |
| | | Ethanol | | | | | | (50)/600 | |
| Castor | Batch reactor of stainless steel, 11/– | Methanol | 10:1–70:1 | – | 200–350 | 20 | 350 °C, 40:1 | (≈100)/30 | [162] |
| Linseed | | Ethanol | 10:1–70:1 | | 200–350 | 20 | 350 °C, 40:1 | (≈100)/40 | |
| Castor | Tubular rector, 7/– | Methanol | 2:1–10:1 | Novozyme 435 in SC $CO_2$, 20 | | 30–70 | 50 °C, 5:1 | (≈50)/12 | [162] |
| | | Ethanol | 2:1–10:1 | | | 30–70 | 40 °C, 5:1 | (≈37)/12 | |
| Fodder radish (*R.sattivus*) | Tubular reactor, 32/– | Methanol<br>Ethanol | 39:1<br>32:1–52:1 | – | 298–336<br>310–325 | 10–18.3<br>9–14 | 317 °C, 18.3 MPa, 39:1<br>319 °C, 12.5 MPa, 39:1 | 97/27<br>97.5/22 | [163] |
| Cottonseed | Cylindrical autoclave, – | Methanol<br>Ethanol | 41:1<br>41:1 | – | 230,250<br>230,250 | | 250 °C<br>250 °C | (≈98)/8<br>(≈86)/8 | [61] |
| Linseed | Cylindrical autoclave, – | Methanol<br>Ethanol | 41:1<br>41:1 | – | 230,250<br>230,250 | | 250 °C<br>250 °C | ≈98/8<br>≈86/8 | [9] |

[a] Two-step process.
[b] v/v.

of biodiesel (90.5%) with the best properties was obtained [156]. With increasing the catalyst loading, the reaction rate increases sharply up to the maximum value and then stays constant. Also, the increase of the reaction temperature has a favorable influence on the FAME yield.

Biodiesel can be also synthesized enzymatically from non-edible oils and methanol or ethanol in the presence of supercritical carbon dioxide [48,162]. The optimum conversion of only about 50% is obtained under supercritical conditions in the presence of lipase Novozym 435. This is a much lower yield than that obtained by supercritical methanol/ethanol esterification. Further, working with jatropha oil, Rathore and Madras [161] have reported that the conversion of jatropha oil is lower with methanol than with ethanol, due to the denaturing effect of methanol on the enzyme. However, working with castor oil, Varma and Madras [162] have shown completely contrary results.

## 4. Optimization of non-edible oils transesterification

### 4.1. The statistical optimization of non-edible oils transesterification

Since the efficiency of FAAE synthesis depends on the applied reaction conditions, it is of great importance to investigate their influence on the esters yield in order to determine the optimal. The classic way of investigation by varying one process variable while others are hold constant are time-consuming and expensive. Instead, the statistical methods, known as design of experiments, are frequently used as a power tool for the process optimization in the past decade such as the response surface methodology (RSM) combined with the central composite rotatable design [39,85,95], factorial design $2^3$ [86], Box–Behnken factorial design [98,99] or the combination of fractional factorial and Doehlert experimental design [91], as well as Taguchi technique [102] and generic algorithm coupled with artificial neural network [45]. These methods estimate not only the effects of individual process variables but also the interactions between them, thus allowing a better knowledge of the process, determining the optimal levels of the process variables and developing more economic and more efficient processes.

According to da Silva et al. [85,86], the catalyst loading, the alcohol:oil molar ratio and their interactions have the greatest impact on the FAEE yield, while the effects of the reaction temperature and the interaction temperature-catalyst loading were not significant. Cavalcante et al. [95] have reported that the ethanol:castor oil molar ratio, the potassium hydroxide catalyst loading, the reaction time, as well as the interaction between KOH loading and reaction time, are effective on the esters yield in both linear and quadratic model at the 95% confidence level. The catalyst loading influences the ester yield in a negative manner. Valle et al. [91] have carried out a comprehensive study on the influence of the process variables on the *Raphanus sativus* ethyl esters yield. In first stage, using a $2^{(5-1)}$ fractional factorial design, they established, contrary to other researchers, that the ethanol:oil molar ratio in the range 6:1–14:1 had no significant influence on the esters yield, while the most significant variable was agitation intensity, which affected the reaction negatively. The reaction time, reaction temperature and catalyst loading were studied in the next stage using the Doehlert design of experiments. The reaction time and quadratic term of reaction temperature positively influence FAEE yield, while the reaction temperature and the quadratic term of catalyst loading have the negative effect on the process. The optimal reaction conditions for achieving the maximum biodiesel yield are usually obtained by using the RSM and the mathematical model coming out from the optimization study [85,86,91,95].

The two-step process of biodiesel synthesis from non-edible oil is rarely statistically optimized. Tiwari et al. [39] optimized the methanol:oil molar ratio, $H_2SO_4$ loading and reaction time for FFA content reduction in the first step, and methanol:oil molar ratio and reaction time for the methanolysis of pretreated oil in the second step. Based on quadratic polynomial model, linear and quadratic terms of all variables and the interaction between methanol:oil molar ratio and catalyst loading were significant in reducing the acid value. The FAME yield was affected by linear and quadratic terms of methanol:oil molar ratio and reaction time, as well as by their interaction. In the optimization of two-step karanja biodiesel synthesis under microwave irradiation, Kamath et al. [99] considered methanol:oil molar ratio, catalyst loading and irradiation time. The statistically significant terms in reducing FFA content were linear and quadratic terms of all variables, the most important factor being catalyst loading, which affected the FFA content negatively. The most important factors affecting FAME yield in the second process step are methanol:oil molar ratio, catalyst loading, interaction methanol:oil molar ratio-irradiation time as well as quadratic terms of all variables, having a negative effect on the FAME yield. Based on polynomial model and RSM, the optimal reaction conditions for both steps were established, and predicted results were validated experimentally. Only Liao and Chung [98] optimized the methanol:oil molar ratio, NaOH amount and flow rate for a continuous microwave assisted methanolysis of jatropha oil using Box–Behnken factorial design. The significant effect on FAME yield had all three variables, interactions between the catalyst loading and the methanol:oil molar ratio and between the catalyst amount and the flow rate, as well as the quadratic term of the catalyst amount. Based on the RSM methodology, the maximum FAME yield was found to be 99.36% under the following optimal reaction conditions: methanol:oil molar ratio of 10.74:1, NaOH amount of 1.26% and flow rate of 1.62 mL/min. Yusup and Khan [102] studied the influence of the methanol:oil molar ratio, reaction temperature and KOH loading on the base-catalyzed methanolysis of acid treated blend of crude palm/crude rubber seed oil, and the optimal combination for maximizing FAME yield were established by using Taguchi technique. For identifying the optimal reaction parameters (methanol:oil molar ratio, catalyst loading and the reaction time) for reducing FFA content in mahua and simarouba oil by an acid-catalyzed pretreatment, Jena et al. [45] developed a generic algorithm method based on an artificial neural network model.

The statistical methods of optimization have been rarely applied in heterogeneously catalyzed, lipase-catalyzed and non-catalyzed alcoholysis reactions. A few studies deal with the optimization of heterogeneously catalyzed methanolysis. An orthogonal test was designated to investigate the influence of the reaction variables on the jatropha oil methanolysis catalyzed by CaO [116]. The order of the reaction variables' effect on the FAME yield was as follows: catalyst loading > reaction time > reaction temperature > methanol:oil molar ratio. Olutoye and Hameed [115] statistically evaluated the FAME production from crude jatropha oil using aluminum oxide modified Mg-Zn catalyst. All investigated reaction variables (methanol:oil molar ratio, catalyst loading and reaction temperature) influenced the FAME yield. The optimization of jatropha oil methanolysis catalyzed by KSF clay and Amberlyst 15 was performed using a $2^3$ full factorial central composite rotatable design [110]. The empirical models for FAME yield as a function of reaction temperature, methanol:oil molar ratio and catalyst loading were developed. In the case of KSF catalyzed methanolysis, the reaction temperature, the methanol:oil molar ratio and their interaction had a significantly positive effect on the FAME yield, while catalyst loading had a negative effect. All three variables positively influenced FAME yield in by Amberlyst 15 catalyzed methanolysis, but interaction between temperature and catalyst loading was significantly negative. The optimum reaction conditions for achieving the

highest FAME yield were established, and the predicted FAME values were in agreement with the experimentally obtained data (Table 6) confirming the model accuracy.

The RSM based on central composite design was used by Su et al. [143], who investigate the influence of five important reaction variables for FAME production from jatropha oil using diethyl carbonate as acyl acceptor and Novozym 435 lipase as a catalyst. The reaction time, reaction temperature, lipase amount and diethyl carbonate:oil molar ratio, as well as the interaction between temperature and amount of added water had a significant positive effect on the FAME yield. The amount of added water and the quadratic terms of all variables except the lipase amount had a significant but negative effect on the esters production. The optimal values of process variables were estimated by solving the regression equation. The predicted FAME yield under optimal reaction conditions was 97.7%, which agreed well with the experimentally obtained yield of 96.2%. De Oliveira et al. [49] optimized the reaction temperature, water amount, enzyme concentration and ethanol:oil molar ratio for castor oil ethanolysis catalyzed by Novozym 435 and Lipozyme IM lipases by applying the Taguchi experimental design. In the case of Lipozyme IM catalyzed ethanolysis, the water amount, linear and quadratic terms of ethanol:oil molar ratio and interactions of enzyme concentration with both the reaction temperature and ethanol:oil molar ratio were effective on the FAEE yield but all with a negative effect, while only the enzyme concentration had a positive effect. Regarding the system catalyzed by Novozym 435, only the water amount had a negative effect, while others linear terms, the quadratic term of ethanol:oil molar ratio and interactions between temperature and water amount and temperature and ethanol:oil molar ratio were statistically significant in a positive manner. The regression equation predicted optimal reaction conditions under which the predicted FAEE yield (82% and 99.6%) agreed well with the experimentally values of 81.4% and 98% for Novozym 435 and Lipozyme IM, respectively.

Valle et al. [163] optimized non-catalyzed ethanolysis and methanolysis of *Raphanus sativus* L. oil using the Doehlert design with three and two variables, respectively. Based on the quadratic regression model, the ethanol:oil molar ratio is the most important factor influencing the reaction negatively, followed by the reaction time and temperature, both having a positive effect. The statistically significant influence on the FAEE yield had the interaction between reaction time and temperature and the quadratic term of ethanol:oil molar ratio, both in a negative manner. The studies of methanolysis showed that the reaction temperature and reaction time, as well as the interaction between them had a statistically significant and positive effect on the FAME yield. The optimal reaction conditions were established based on the RSM and model equation. The RSM model was used for the optimization of the subcritical hydrolysis of jatropha oil, obtained by the supercritical $CO_2$ extraction of *Jatropha curcas* kernels, and the supercritical methylation of the hydrolyzed oil [159]. In this study, two (reaction temperature and reaction time) and three (reaction time, methanol:FFA volume ratio and reaction temperature) factors were statistically evaluated for oil hydrolysis and methylation of the hydrolyzed oil, respectively. The both factors were effective on the oil hydrolysis. In the supercritical methylation process, the reaction temperature and reaction time had a positive effect while the methanol:FFA volume ratio had a negative effect on the FAME yield [159]. Chen et al. [160] optimized the subcritical hydrolysis of *Jatropha curcas* crude seeds oil and the supercritical methylation of the hydrolyzed oil. The highest FFA yield was obtained at 290 °C in 60 min under 11 MPa, at water:oil volume ratio of 10:1 and acetic acid amount of 2.5 vol.%. The optimum conditions for the supercritical methylation process (3:1 methanol:FFA volume ratio, 290 °C and 9 min) resulted in the FFA conversion of 98.3%.

Shuit et al. [164] statistically evaluated the production of FAME in a reactive extraction process of *Jatropha curcas* L. seeds using RSM coupled with central composite design. Four different process variables, namely reaction temperature (30–60 °C), methanol:seed ratio (5–20 mL/g), $H_2SO_4$ loading (5–30 wt.%) and reaction time (1–24 h) were optimized. All variables, as well as the interaction between reaction temperature and catalyst loading significantly affect the FAME yield in a positive manner, the most important factor being the catalyst loading. The significant effect of $H_2SO_4$ was explained by its role of catalyst not only in the reactive extraction process but also in accelerating the oil extraction due to a better solubility of lipid and oil in the acidic solvent. Based on the regression model, the highest FAME yield of 99.8% could be obtained with the following process variables: reaction temperature of 60 °C, methanol:seed ratio of 10.5 mL/g, 21.8% of $H_2SO_4$ and reaction time of 10 h.

### *4.2. The kinetics of non-edible oils transesterification*

The alcoholysis reaction kinetics is indispensable for the production process development and the reactor design, operation and scale-up. The fundamental understanding of the alcoholysis reaction kinetics is necessary for development of mathematical models describing the reaction rate and the product yield. The kinetic studies provide parameters that are used for prediction of the reaction progress under particular reaction conditions, process analysis and control.

In the studies of the homogeneous catalyzed methanolysis two stages are well-recognized: initial heterogeneous stage controlled by the mass transfer rate and a pseudo-homogeneous stage which is chemically controlled. The initial stage is caused by the incomplete miscibility of the nonpolar and polar reactants, and it is observed at lower reaction temperatures and agitation intensities. The mass transfer limitations have been included in modeling the overall process kinetics only in a few studies of edible oils methanolysis [165,166]. Karmee et al. [82] noticed that the oily feedstock, alcohol and catalyst could qualitatively alert the kinetics of alcoholysis reaction. In the case of jatropha oil, the methanolysis reaction was quite rapid especially at the early reaction stage, compared to mahua and the edible oils [78].

The kinetics of the homogeneously catalyzed alcoholysis reaction has been most frequently studied, and different kinetic models were used (Table 10). Some complex models are based on the stepwise reversible alcoholysis reaction [82,167] and sometimes include side saponification reactions [76]. However, there are simple models that assume the irreversible overall reaction [51,78,86]. Bikou et al. [167] studied the effect of water content in ethanol on the cottonseed oil ethanolysis reaction kinetics. The dependence of both the reaction rate and equilibrium constants are well correlated. This result allows assessing if it is preferable to use anhydrous, high-price ethanol or ethanol containing a certain amount of water. For the pongamia oil methanolysis, Karmee et al. [82] observed that the fastest reaction was the forward reaction of the first step (methanolysis of TAG to diacylglycerols, DAG), while the second step (reaction of DAG to monoacylglycerols MAG) was the slowest step. The most complex kinetics model, which includes saponification reactions of all glycerides and esters, was developed for the methanolysis of a jatropha oil–waste food oil mixture [76]. The comparison of the second-order kinetics based on the stepwise methanolysis reaction, and the new proposed kinetic model showed that the latter had smaller deviation from experimental data.

Development of simple kinetic models which fitted well experimental data is favorable, because they do not require complex computation of their parameters. The overall reaction of castor oil ethanolysis in the kinetically controlled region was described by

**Table 10**
A survey on the reaction mechanism and kinetics model of homogeneously catalyzed alcoholysis of non-edible oils.

| Feedstock (oil) | Alcohol | Temperature, °C | Reaction mechanism | Kinetics model[c] | Reference |
|---|---|---|---|---|---|
| Pongamia | Methanol | 60 | Three consecutive reversible reactions | $-\frac{d[TAG]}{dt} = k_1[TAG][MeOH] - k_{-1}[DAG][FAME]$<br>$-\frac{d[DAG]}{dt} = k_2[DAG][MeOH] - k_{-2}[MAG][FAME] - k_1[TAG][MeOH] + k_{-1}[DAG][FAME]$<br>$-\frac{d[MAG]}{dt} = k_3[MAG][MeOH] - k_{-3}[Gl][FAME] - k_2[DAG][MeOH] + k_{-2}[MAG][FAME]$ | [82] |
| Cottonseed[a] | Ethanol | 78.2 ± 2 | Three consecutive reversible reactions | $-\frac{d[TAG]}{dt} = k_1[TAG][EtOH]^3 - k_{-1}[DAG][FAEE]$<br>$-\frac{d[DAG]}{dt} = k_2[DAG][EtOH]^3 - k_{-2}[MAG][FAEE] - k_1[TAG][EtOH]^3 + k_{-1}[DAG][FAEE]$<br>$-\frac{d[MAG]}{dt} = k_3[MAG][EtOH]^3 - k_{-3}[Gl][FAEE] - k_2[DAG][EtOH]^3 + k_{-2}[MAG][FAEE]$ | [167] |
| Jatropha<br>Mahua | Methanol | 28 and 45 | One step reaction (overall reaction) | $-\frac{d[TAG]}{dt} = k[TAG]^2[MeOH]$ | [78] |
| Cottonseed[b] | Methanol | 60 | One irreversible reaction (overall reaction) | $-\frac{d[TAG]}{dt} = k[TAG]$ | [51] |
| | Ethanol | 80 | | | |
| Castor | Ethanol | 30–70 | One irreversible reaction (overall reaction) | $-\frac{d[TAG]}{dt} = k[TAG]$ | [86] |
| Jatropha–waste food oil mixture | Methanol | 50 | Three consecutive reversible (methanolysis) + five saponification reactions | $\frac{d[TAG]}{dt} = [OH](-k_1[TAG][MeOH] + k_{-1}[DAG][FAME] - k_5[TAG])$<br>$\frac{d[DAG]}{dt} = [OH](k_1[TAG][MeOH] - k_{-1}[DAG][FAME] - k_2[DAG][MeOH] + k_{-2}[MAG][FAME] + k_5[TAG] - k_6[DAG])$<br>$\frac{d[MAG]}{dt} = [OH](k_2[DAG][MeOH] - k_{-2}[MAG][FAME] - k_3[MAG][MeOH] + k_{-3}[Gl][FAME] + k_6[DAG] - k_7[MAG])$<br>$\frac{d[Gl]}{dt} = [OH](k_3[MAG][MeOH] - k_{-3}[Gl][FAME] + k_7[MAG])$<br>$\frac{d[FAME]}{dt} = -\frac{d[MeOH]}{dt} = [OH](k_1[TAG][MeOH] - k_{-1}[DAG][FAME] + k_2[DAG][MeOH] - k_{-2}[MAG][FAME]$<br>$+k_3[MAG][MeOH] - k_{-3}[Gl][FAME] - k_4[FAME])$<br>$\frac{d[OH]}{dt} = -\frac{d[A]}{dt} = [OH](-k_4[FAME] - k_5[TAG] - k_6[DAG] - k_7[MAG] - k_8[FFA])$<br>$\frac{d[W]}{dt} = -\frac{d[FFA]}{dt} = -k_8[FFA][OH]$ | [76] |
| Pre-esterified jatropha oil | Methanol | 32–51 | One irreversible reaction (overall reaction) | $-\frac{d[TAG]}{dt} = k[TAG]^2$ | [136] |

[a] In the presence of water.
[b] Using both mechanical stirring and low frequency ultrasound.
[c] [TAG], [DAG], [MAG], [FAME], [FAEE], [MeOH], [EtOH], [Gl], [FFA], [OH], [A], [W] – concentrations of TAG, DAG, MAG, FAME, FAEE, methanol, ethanol, glycerol, FFA, $OH^-$, soap and water, respectively, $t$ – time, $k_1$, $k_2$ and $k_3$ – forward alcoholysis reaction rate constant, $k_{-1}$, $k_{-2}$ and $k_{-3}$ – reverse alcoholysis reaction rate constant, $k$ – overall reaction rate constant, $k_4$, $k_5$, $k_6$, $k_7$, $k_8$ – saponification reactions rate constants.

the irreversible first-order kinetic model with respect to acylglycerols and its activation energy, in the temperature range 30–70 °C, was 70.6 kJ/mol [86]. Lu et al. [136] established a pseudo second-order kinetic model with respect to TAG for the base-catalyzed methanolysis of pre-esterified jatropha oil with activation energy of 15.46 kJ/mol in the temperature range between 32 and 51 °C. For the base-catalyzed methanolysis of cottonseed oil, using both mechanical stirring and low frequency ultrasound, the first and second order reactions with respect to TAG were reported, although a better fit was obtained for the former [51]. Exceptionally, Jain and Sharma [97] studied the kinetic of both steps in the acid-base catalyzed transesterification of jatropha oil with respect to FAME:

$$\frac{d[\mathrm{FAME}]}{dt} = k[\mathrm{FAME}] \tag{1}$$

where [FAME] is the FAME concentration, $t$ is time and $k$ is rate constant. Based on the rate constant values for esterification and methanolysis reactions it was observed that the esterification reaction was slower than the methanolysis. The activation energy of methanolysis reaction in the temperature range 35–60 °C was found to be 87.81 kJ/mol [97].

The reaction mechanism of heterogeneously catalyzed reactions is more complex and includes various reactions that occur with the solid catalyst. The kinetics of heterogeneously catalyzed alcoholysis has been rarely studied, and the various kinetic models have been reported. The kinetics of different vegetable oils methanolysis over heteropolyacids supported on K-10 clay in the kinetically controlled region was described by three consecutive, reversible, second-order reactions as follows [120]:

$$\begin{aligned} -\frac{d[\mathrm{TAG}]}{dt} &= w(k_1[\mathrm{TAG}][\mathrm{MeOH}] - k_{-1}[\mathrm{DAG}][\mathrm{FAME}]) \\ \frac{d[\mathrm{DAG}]}{dt} &= w(k_1[\mathrm{TAG}][\mathrm{MeOH}] - k_{-1}[\mathrm{DAG}][\mathrm{FAME}] \\ &\quad -k_2[\mathrm{DAG}][\mathrm{MeOH}] + k_{-2}[\mathrm{MAG}][\mathrm{FAME}]) \\ \frac{d[\mathrm{MAG}]}{dt} &= w(k_2[\mathrm{DAG}][\mathrm{MeOH}] - k_{-2}[\mathrm{MAG}][\mathrm{FAME}] \\ &\quad -k_3[\mathrm{MAG}][\mathrm{MeOH}] + k_{-3}[\mathrm{Gl}][\mathrm{FAME}]) \end{aligned} \tag{2}$$

where [MAG], [DAG] and [TAG] are the concentrations of MAG, DAG and TAG, [MeOH] is the concentration of methanol, [FAME] is the concentration of FAME, $w$ is the catalyst loading, $t$ is time and $k_i$ and $k_{-i}$ are rate constant of forward and reverse reactions, respectively ($i$ = 1, 2 and 3). The experimental data were fitted well with the kinetic model, but the kinetic parameters for all used oils were not reported. The same model was applied for the jatropha oil methanolysis in the presence of KSF clay and Amberlyst 15. The experimental data were agreed well with the kinetic model, but no kinetic parameters were published [110]. Vyas et al. [113] and Zięba et al. [123] established simpler kinetic models for jatropha and castor oil methanolysis over $KNO_3/Al_2O_3$ and $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$ catalyst, respectively. In order to fit the experimental data better, Vyas et al. [113] assumed that the overall reaction followed $n$th order:

$$-\frac{d[\mathrm{TAG}]}{dt} = k[\mathrm{TAG}]^n \tag{3}$$

The best fit was obtained for $n \approx 0.5$. The activation energy for reaction carried out at 50–70 °C was estimated to be 112.8 kJ/mol. The overall reaction rate of the castor oil methanolysis, due to the excess of methanol, followed the pseudo-first order kinetics with respect to TAG and the apparent activation energy was calculated to be 73.3 kJ/mol in the temperature range from 20 to 60 °C [123].

For the enzyme-catalyzed alcoholysis, only a limited number of kinetic studies are found in the literature. Generally, the most commonly used model to describe the kinetics of FAAE synthesis using lipases as a catalyst is the Ping Pong Bi-Bi mechanism with competitive alcohol inhibition [168–171]:

$$v_i = \frac{V_{\max}[\mathrm{TAG}][\mathrm{A}]}{K_{m,\mathrm{TAG}}[\mathrm{A}](1 + [\mathrm{A}]/K_{i,\mathrm{A}}) + K_{m,\mathrm{A}}[\mathrm{TAG}] + [\mathrm{TAG}][\mathrm{A}]} \tag{4}$$

where are $v_i$ – initial rate, $V_{\max}$, $K_{m,\mathrm{TAG}}$, $K_{m,\mathrm{A}}$ and $K_{i,\mathrm{A}}$ – kinetic constants, [TAG] and [A] – concentrations of TAG and acyl acceptor, respectively. Considering the interesterification of TAG and methyl acetate for biodiesel production, Xu et al. [171] also developed a three-consecutive reversible-reaction kinetic model (shown by Eq. (2)) and reported that the first step, i.e. reaction TAG to DAG, was the rate-limiting step for the overall reaction. Torres et al. [172,173] proposed the modified Michaelis–Menten mechanism that incorporates or not the reaction reversibility and the enzyme deactivation, depending on the lipase source.

Up to date, the kinetics of enzyme-catalyzed non-edible oils alcoholysis has hardly been studied. The kinetics of the castor oil ethanolysis in supercritical carbon dioxide [162] and the cottonseed oil methanolysis in the presence of ectoine [145] catalyzed by Novozym 435, was described by the Ping Pong Bi-Bi mechanism with competitive alcohol inhibition (Eq. (4)). By studying the effect of temperature on the initial reaction rate, Royon et al. [142] calculated the lumped activation energy of 19 ± 2 kJ/mol that corresponded to the forward first stepwise reaction of the cottonseed oil methanolysis.

Under supercritical conditions, the reaction mixture becomes a single homogeneous phase without mass transfer limitations that accelerates the reaction rate. The reaction rate of supercritical alcoholysis depends on the composition of the vegetable oil and the used alcohol. Oils containing TAG of saturated fatty acids react faster than oils with TAG of unsaturated acids, and the reaction becomes slower with an increasing number of double bonds in the unsaturated acids [161,162]. The alcoholysis reaction rate of castor oil containing a high level of ricinoleic acid, a hydroxy fatty acid, cannot be compared with those of other vegetable oils [162]. Generally, the kinetic analyses of the supercritical alcoholysis up to date assumed one-step reaction and the pseudo first-order reaction kinetics with respect to TAG [156,157,159–162]:

$$-\frac{d[\mathrm{TAG}]}{dt} = k[\mathrm{TAG}] \tag{5}$$

The activation energies for jatropha and pongamia oil methanolysis and ethanolysis at temperatures range 200–400 °C were calculated to be between 9.1 and 11.4 kJ/mol [161], which were lower than those determined for the castor oil methanolysis and ethanolysis (35 and 55 kJ/mol, respectively) in almost the same temperature interval [162]. There was no obvious discontinuity near the critical temperature. Tang et al. [156] established a pseudo first-order reaction kinetics with respect to all glycerides species (TAG, DAG, MAG) and FFA for the jatropha oil methanolysis catalyzed by micro-NaOH with activation energy of 84.1 kJ/mol in the temperature range 250–275 °C. The jatropha oil transesterification via supercritical methyl acetate in the temperature range 300–345 °C was described by the pseudo first-order reaction kinetics with respect to TAG [157]. The higher value of calculated activation energy for this process (364 kJ/mol) indicates that methyl acetate is less reactive in comparison with methanol or ethanol. Chen et al. [159,160] studied the kinetic of FAME synthesis using subcritical hydrolysis and subsequent supercritical methanolysis of jatropha oil extracted from seeds and kernels in the temperature range from 250–290 °C. The both steps follow the pseudo first-order reaction kinetics with respect to TAG. For jatropha seed and kernel oil, the calculated activation energies for hydrolysis were 50.2 and 68.5 kJ/mol, and for methanolysis 23.9 and 45.2 kJ/mol, respectively. The higher value of activation energy for the hydrolysis indicated that this reaction was the rate determining step for biodiesel production, but the

difference between the activation energies of methanolysis reaction of seed and kernel oil was not explained by the authors.

### 4.3. The possibilities for improvement of non-edible oils transesterification

The improvement of the alcoholysis reaction includes all activities that increase the ester yield, shorten the reaction time and/or simplify the process. Several different novel methods have been used in the last decade to improve the biodiesel production from non-edible oils such as the application of in situ transesterification processes, ultrasonic irradiation, microwave heating and co-solvent.

#### 4.3.1. In situ processes

Using conventional methods, a non-edible oil is directly treated with an alcohol in the presence of a catalyst. Therefore, the total process involves various oil treatments such as its extraction, purification, esterification and/or transesterification. The novel in situ technology for producing biodiesel from non-edible oils with high FFA content involves only one step to finish all necessary stages. Including both extraction and esterification/transesterification, this technology is known as reactive extraction. The alcohol acts as both an extracting solvent and an esterification/transesterification reagent. Once the oil is extracted out from seeds, it is converted to esters. In this way, it is possible to reduce processing time, solvent amount and total cost. However, it requires a higher amount of alcohol than traditional processes.

Several researchers have studied in situ biodiesel production from non-edible oil bearing materials in the absence of a catalyst [174] and the presence of an acid [101,164,175], a base [51] or an enzyme [152,176] catalyst. A review of in situ catalytic and non-catalytic biodiesel production processes oil from non-edible seeds is given in Table 11. The use of base catalysts is more favorable than acid ones. Georgogianni et al. [51] produced esters by base-catalyzed in situ process from cottonseeds with the oil containing a low FFA amount employing both mechanical agitation and ultrasonication. In the presence of FFA in a high content, the use of a base catalyst leads to the well-known problems of soap formation and difficulty in product separation [164]. The use of an acid catalyst in an in situ one-step process in the biodiesel production from jatropha seeds increases the ester yield up to 99.8% [164,175], compared to the conventional two-step acid/base [96], two-step enzymatic or in situ enzymatic [152,176] process. In the last case, the yield improvement by the lipase-catalyzed in situ reactive extraction with respect to the two-step extraction/lipase-catalyzed transesterification was 5.3% [176] or 31.7% [152]. Although the required reaction time for the optimum ester yield is in the range from 10 to 24 h, which is longer compared to conventional transesterification processes, it should be noted that in reactive extraction, both extraction and transesterification occur simultaneously. Unlike reports for jatropha seeds [152,164,175,176], the conversion in the case of other vegetable species such as castor was lower for the reactive extraction than for conventional methods [101].

The highest FAME yield was achieved from jatropha seeds by employing non-catalytic supercritical reactive extraction at high-pressure conditions [174]. The 103.5% of FAME yield exceeds the theoretical one because of the excess of extracted oil. The co-solvent is effective at the beginning of the process and the supercritical fluid extraction dominates at higher temperatures, which brings the total oil extraction efficiency to 100%. The effect of co-solvent was more evident in the in situ catalytic process than in the conventional one in the cases of jatropha [175] and castor red [101] seeds. The co-solvent can facilitate the diffusion of the alcohol through the particles of the seeds. However, this phenomenon was not observed with nordestina variety castor seeds, where the conversion with ethanol is higher than that with the solvent mixture [101].

The use of ultrasonic energy improves in situ transesterification process in base-catalyzed biodiesel production from cotonseed [51]. The increase in esters yield was obtained in a remarkably short time (20 min and 40 min in reactions with methanol and ethanol, respectively), and the yields of the isolated esters were higher for the ultrasonicated reaction system than for the mechanically stirred system [51].

The efficiency of oil extraction from seeds of different size increases gradually with the progress of the reactive extraction process [175]. The size of seeds is a significant factor affecting the ester yield. Higher oil extraction efficiencies were achieved from smaller seeds, due to a larger contact surface area and a less hindrance from the outer shell covering the oil seeds [174,175]. The oil extraction from the seeds is favor until the efficiency reaches more than 90%. For larger seeds, there is a stage where mass transfer limitation exists. Also, they settle-down easer and reduce the methanol:oil contact surface area for the transesterification process.

#### 4.3.2. The use of ultrasonic irradiation

The use of ultrasonic irradiation is a new, more efficient mixing method in biodiesel production, compared to conventional methods of agitation. The ultrasonic energy improves the mass transfer between the immiscible reactants, increases the chemical reaction rate and ester yield and decreases the reaction time and energy consumption. Deng et al. [77] concluded that two-step process coupled with ultrasonic irradiation is an efficient method for biodiesel production from crude jatropha oil with high FFA value. They showed that the high FAME yield (96.4%) can be achieved in only 30 min (Table 5). Ultrasound-assisted base catalyzed ethanolysis of cottonseed oil under optimal reaction conditions gives 90% ester yield in 60 min, while in the case of mechanical agitation only 86% ester yield is obtained for the same time [51] (Table 4). This can be explained assuming that soap formation is reduced in the presence of ultrasound action [51]. Ultrasonic irradiation is also effective in increasing the ester yield in the in situ biodiesel production from cottonseeds [51] (Table 11) and race bran [177].

#### 4.3.3. The use of microwave heating

Microwave irradiation is an efficient heating method used to reduce the reaction time and to improve the ester yield in the transesterification reaction of non-edible oils. Its advantages are simplicity, low cost and energy economy [50,99,127]. Heat is generated during this process by molecular friction, because polar alcohol molecules align with the continuously changing magnetic field generated by microwaves. The increase of the reaction rate is attributed to an enhanced temperature at the catalytic surface [50]. Because of the effective heat transfer, processes with microwave irradiation can be completed in a much shorter time than those with conventional heating [50,99]. Microwave irradiation seems to have a strong effect on the reaction rate rather than on the ester yield [99]. Comparing the base catalyzed methanolysis of cottonseed oil under microwave and conventional heating at 60 °C, Azcan and Danisman [50] observed approximately the same ester yields in both processes in 7 min and 30 min, respectively. The reaction rate of microwave-assisted reaction of karanja oil with methanol increases drastically, which reduces the reaction time to 2–3 min, compared to 1–2 h in the case of conventional heating [178]. Identical FAME yields are achieved by homogeneously and heterogeneously acid-catalyzed transesterification under microwave radiation [126]. There are contradictory conclusions on the reactivity of methanol and ethanol under microwave irradiation. While Yuan et al. [126] observed that the methanol system achieved the equilibrium in 1 h and was twice as fast as the ethanol system. Perin et al. [125] achieved the same biodiesel yield in a shorter

**Table 11**
A review of the in situ transesterification of different non-edible feedstocks.

| Feedstock (oil) | Type, volume of reactor, $cm^3$/Type of agitator, agitation intensity, rpm | Acyl acceptor | Alcohol to seed ratio, mL/g | Catalyst/loading, wt.% to the seed | Temperature, °C | Optimal reaction conditions | | Reference |
|---|---|---|---|---|---|---|---|---|
| | | | | | | Reaction conditions | Oil extraction efficiency/yield (conversion), %/Time, h | |
| Jatropha | Flask, 250/Magnetic, – | Methanol | 7.5 | $H_2SO_4$/1 | 60 | | 91.2/99.8[a]/24 | [175] |
| | Flask, 500/Magnetic, – | Methanol | 5–20 | $H_2SO_4$/5–30 | 30–60 | 60 °C, 10.5 mL/g, 21% $H_2SO_4$ | 98.1/10 | [164] |
| | Batch reactor, 450/Mechanical, 400 | Methanol | 10 | – | 200–300 | 300 °C | 103.5[b]/24 | [174] |
| | Screw-caped glass vials/–, 180 | Methyl-acetate | 5–20 | Novozym 435/30 | 50 | 7.5 mL/g | 86.1/24 | [176] |
| | | Ethyl-acetate | | | | | 87.2/24 | |
| | Screw-caped glass vials/–, 180 | Dimethyl carbonate | 5–20 | Novozym 435/10 | 50 | 10 mL/g | 95.9/24 | [152] |
| | | Diethyl carbonate | | | | | 94.5/24 | |
| Castor | Flask, 100/Mechanical, 300 | I step: Ethanol | 40:1[c] | $H_2SO_4$/1 | 60 | | – | [101] |
| | | II step: Ethanol | 20:1[c] | KOH/1 | 60 | | (51.2)/1 and (65.6)[d]/1 | |
| Cottonseed | Batch reactor, 500/Mechanical, 600 and ultrasound | Methanol | 7:1 | NaOH/2 | 60 | | 97/2, 97/0.67[e] | [51] |
| | | Ethanol | 7:1 | NaOH/2 | 80 | | 78/6, 98/0.67[e] | |
| Rice bran | | Methanol | 10:1 | $H_2SO_4$/27.6 | 60 | | 82.79[f]/6 (medium FFA content of 47.87%) 79.08/6 (low FFA content of 13.27%) | [177] |

[a] *n*-hexane as co-solvent (10% vol. of methanol).
[b] supercritical conditions: 240 MPa; *n*-hexane as co-solvent (2.5 mL/g of seed).
[c] alcohol:oil molar ratio.
[d] *n*-hexane as co-solvent (20%, v/v to oil).
[e] ultrasonic power: 200 W; frequency: 24 kHz.
[f] ultrasonic power: 500 W; frequency: 35 kHz.

time with ethanol than with methanol. A continuous microwave irradiation reactor was developed by Liao and Chung [98] to convert jatropha oil to alkyl ester. Since the microwave power was set at 80 W and the energy consumption in the 10 min process was about 48 kJ, it was concluded that the ratio of energy consumption to the biodiesel generation would be decreased significantly in the large-scale microwave system.

### 4.3.4. The effect of co-solvent

The use of a co-solvent in the reaction mixture improves miscibility of vegetable oil and alcohol differing in polarities [179], minimizes the induction period [180] and enables the system to overcome the initial mass transfer resistance. The added solvent should be inert and cannot either react with reactants or deactivate the catalyst. By adding a co-solvent to the reaction mixture, the solubility of alcohol in the oil phase increases, an oil-rich single-phase is generated and the reaction rate and the ester yield are enhanced. Tetrahydrofuran (THF), methyl tert-butyl ether (MTBE), dimethyl ether, diethyl ether and *n*-hexane are the most often used co-solvents in the biodiesel production. The THF and *n*-hexane are chosen as co-solvents because of their boiling points close to that of methanol and their easy recovery at the reaction end. THF is a good co-solvent because of its miscibility with methanol and water due to hydrogen bonding. In the presence of THF as co-solvent, the FAME yield in the base catalyzed transesterification of karanja oil is increased up to 95%, compared that of 92% achieved in its absence in the same time [81]. An almost complete conversion (99%) was achieved with THF in the case of mahua oil [78]. However, the use of THF in the case of jatropha oil transesterification appears not to be necessary, especially because of the cost involved in the separation of THF from the reaction mixture. Due to a high reaction rate of jatropha oil, the rate-enhancing effect of THF is less than that in the case of mahua oil [78]. The use of co-solvent is recommended for the reactions performed at lower temperatures when mass transfer effects dominate [78]. When ethanol was used as solvent and *n*-hexane as co-solvent in the two-step transesterification process of castor oil, it was not observed a significant effect on the conversion and the reaction rate [101].

## 5. Conclusions

Because of environmental pollution by fuel combustion emission, an increase of the world energy demand and competition of edible oil sources for human use and biofuel production, the non-edible oils have become the leading raw materials for obtaining biodiesel. Of several possible methods for biodiesel production from non-edible oils, their transesterification reaction with an alcohol in the presence of a catalyst is the most suitable method. Both one- and two-step processes of homogeneously and heterogeneously catalyzed alcoholysis of non-edible oils are used today in the biodiesel synthesis. In the case of one-step processes, the choice between base and acid catalysts mainly depends on the FFA content (or acid value) in the non-edible oil. Base catalysts are preferable in the case of non-edible oils with a lower FFA content, while acid catalysts are suitable to the oils having a high amount of FFAs due to the ability of acid catalyst to simultaneously catalyze esterification and alcoholysis reaction. Two-step (acid/base) processes, employed when non-edible oils have a high FFA content, are an effective method to obtain a high biodiesel yield within a short reaction time. Sometimes, the modified catalysts with dual basic and acidic sites or the mixture of acid and base catalysts are employed with the same goal. The use of solid catalysts instead of homogeneous ones is more desired for many reasons such as reduced environmental pollution and higher qualities of biodiesel and glycerol. However, a completely heterogeneous two-step process has not been developed yet.

The use of immobilized lipases and supercritical conditions for transesterification of non-edible oils are currently among the most promising methods for biodiesel production. Lipases are especially suitable because they can catalyze simultaneously both TAG alcoholysis and FFA esterification. The carrying out in non-aqueous environments, easy recovery of glycerol and the use of feedstock with high FFA content are also the advantages of applying enzymes for biodiesel synthesis from non-edible oils over the other methods. However, the relatively high price of lipases at present is their main drawback for their use on the commercial scale. Compared to conventional methods, the transesterification reaction rate under supercritical conditions is higher, the reaction time is shorter, separation and purification of biodiesel are simply, there is no soap formation and no waste generation from catalyst separation and absence of catalyst makes the glycerol recovery easier.

The use of statistical methods, providing the interactions between variables optimizing the process conditions and allowing better knowledge of the process, contributes to the development of economically efficient processes of biodiesel production based on non-edible plant oils. Mathematical models describing the reaction rate are necessary for understanding the fundamental transesterification kinetics for the reactor design and process scale-up. Not requiring complex computation, simple kinetic models are favorable when fitted well the experimental data. Several different novel methods have been used in the last decade to improve the biodiesel production from non-edible oils. These methods such as the application of in situ transesterification processes, ultrasonic irradiation, microwave heating and co-solvent reduce processing time and energy consumption and enhance the ester yield.

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